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On the Magnetic Susceptibility of Ozone

By

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Cultivation of Science.*

ABSTRACT.

Employing the retorsional method in which the gas surrounds the test rod system, the magnetic susceptibilities of oxygen and ozonised oxygen are investigated. The different sources of error such as the current fluctuations, temperature changes, etc., have been eliminated with great care.

In all cases the magnetic force on the mixture was less than in pure oxygen. By analysing the percentage of the gas during each experiment, and carrying out a number of independent investigations under varying conditions and sensitivity, the most probable sign is deduced.

Calculations are made for the susceptibility of the partial pressure of oxygen and the contribution of ozone is deduced each time. Since the contribution is smaller than the errors, by the method of statistical probability of errors, the gas appears to be diamagnetic.

Introduction.

Becquerel[1] as a result of his investigation on ozonised oxygen, concluded that ozone has a specific paramagnetism of about 3 to 4 times that of oxygen. Later on Schumeister[2] came to similar conclusions. Ozone has an even number of electrons and generally such systems are diamagnetic, oxygen being an anomalous case. It was thus thought important to investigate the problem accurately and decide the magnetic behaviour of ozone. When the work was in progress a paper on the subject appeared in the Proceedings of the National

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[1] Becquerel, Compt. rend., 92, 348 (1881).
[2] Schumeister, Sitz. Akad. Wis. Wein., 11, 83, 45 (1881).

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[1] Becquerel, Compt. rend., 92, 848 (1881).
[2] Schumeister, Sitz. Akad. Wis. Wein., 11, 83, 45 (1881).

Academy of Sciences.[3] Using the Guoy method, it concludes that the paramagnetism of ozone is very small or it is diamagnetic. No mention is made in the paper regarding the temperature fluctuations during the investigation. Since the susceptibility of oxygen depends on temperature, arrangements are made in the present investigation to avoid this source of uncertainty. It is also mentioned in that paper that in some cases, observations in oxygen and the mixture fell at the same points. If we take account of the partial pressure of oxygen, such a coincidence would also seem to indicate a paramagnetism for ozone comparable to that of known paramagnetic gases.

Although Guoy method is accurate for an absolute determination, it is less sensitive to small fluctuations of susceptibility, than a properly set torsion method.

In the following attempt, the different sources of error have been eliminated as far as possible.

The conclusions do not differ much from those of Wulf.[4]

The Torsion Balance.
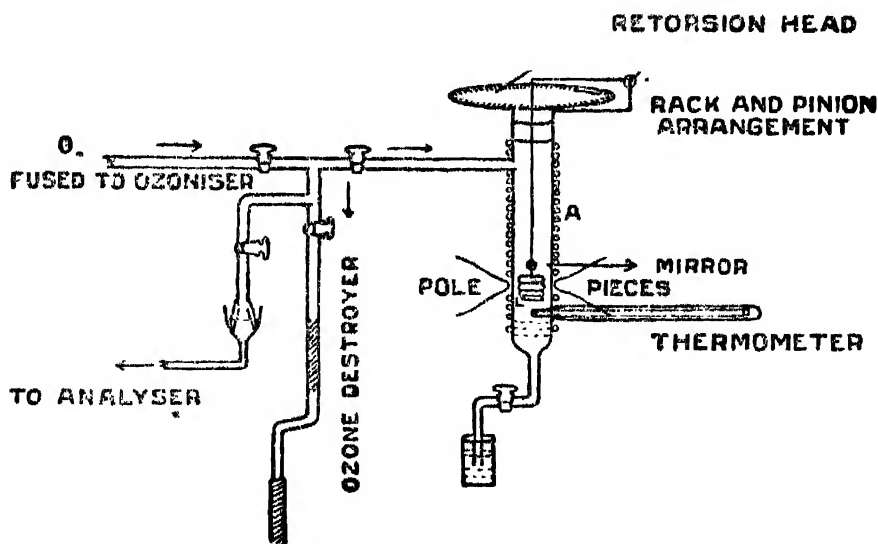
Fig. I.

Wulf. O. R. Proc. N. A. S., 13, 744 (1928).
Wulf., loc. cit.

This is shown diagrammatically in the adjoining figure (Fig. I). For a detailed description of the same, the maintenance of current, temperature, etc., reference may be had to the author's paper " On the Relation of Diamagnetic Susceptibility in the Liquid and Vapour States." [5]

A short description, with the improvements made, is however given below. Since oxygen is a strongly magnetic gas, the force on the same is large, but the balance is to be kept sensitive to record small fluctuations. Thus the retorsion method is employed instead of the torsion, as in the previous investigation.

The retorsion head was of the construction of Adam Hilger and with the vernier, could read accurate to 10 seconds. This was further improved in the laboratory with a worm-wheel arrangement to enable the rotation, without the least bodily disturbance to the balance. The lower circle carrying the vernier has a heavily gilded brass cylinder attached to it. The axial rod of the rotatable scale passes through a perfectly central hole in the cylinder. This cylinder fits the glass tube A and is attached outside with shellac.

The measuring tube system L, suspended in the magnetic field, consists of three closed tubes with a small gold plate attached to the same, for damping the oscillations in the magnetic field. This is surrounded by the gases in question. It is known that the relative retorsion angles in the magnetic field are proportional to the volume susceptibilities of the surrounding media. The maintenance of constant conditions being the most difficult part.

A copper tube is wound round the tube A for temperature maintenance by circulation of water. The thermometer is fused into a side tube, to avoid rubber or other reacting materials. The inlet tube leading to the magnetic balance is fused to the ozoniser system. Ozone could be let to the

[5]   Vaidyanathan, V. I., Ind. Jour. Phys., Vol. II, p. 135 (1928).

balance or destroyer or the analyser without disturbance of the arrangement. Sulphuric acid was employed for lubricating the taps.

In the initial experiments, the ozone destroyer was a glass tube maintained red hot and connected as shown in the figure. This proved very troublesome and afterwards it was changed into a chloroform solution of oleic acid, through which the escaping ozone was allowed to bubble. The mercury seal shown in the diagram connects the analyser.

A gilded phosphor-bronze wire was first employed for the torsion fibre, but its truth began to fail after a few experiments. Subsequently glass fibres were employed. Parts that come in contact with ozone, are only gold, platinum or glass.

Method of Observation.

With a view to obtain an idea of the most probable sign of the magnetic behaviour of ozone and to compare it with the relative sources of error, about 30 independent experiments were carried out with different concentrations varying from traces of ozone up to about 7 per cent., and with varying fields. In a few initial experiments the complete angle was restored in oxygen and independently in ozone. As the complete retorsion was of the order of 5 degrees and the difference in the retorsion angle between pure oxygen and ozone mixture was about 5 minutes, the results were not consistent. In the next series of experiments the spot of light was restored to the original position in pure oxygen and maintaining the field and temperature constant, the current of ozone was turned and the shift alone was restored. The shift on the reflected scale was about 3 to 4 mms. and the exact restoration was also found difficult. In subsequent experiments this shift was directly observed. An accurate calibration over a short region of the scale including that of the shift enabled the corresponding

retorsion angle to be estimated graphically, the calibrations being carried out under the same conditions, as when the experiment was performed.

The ozonisers.
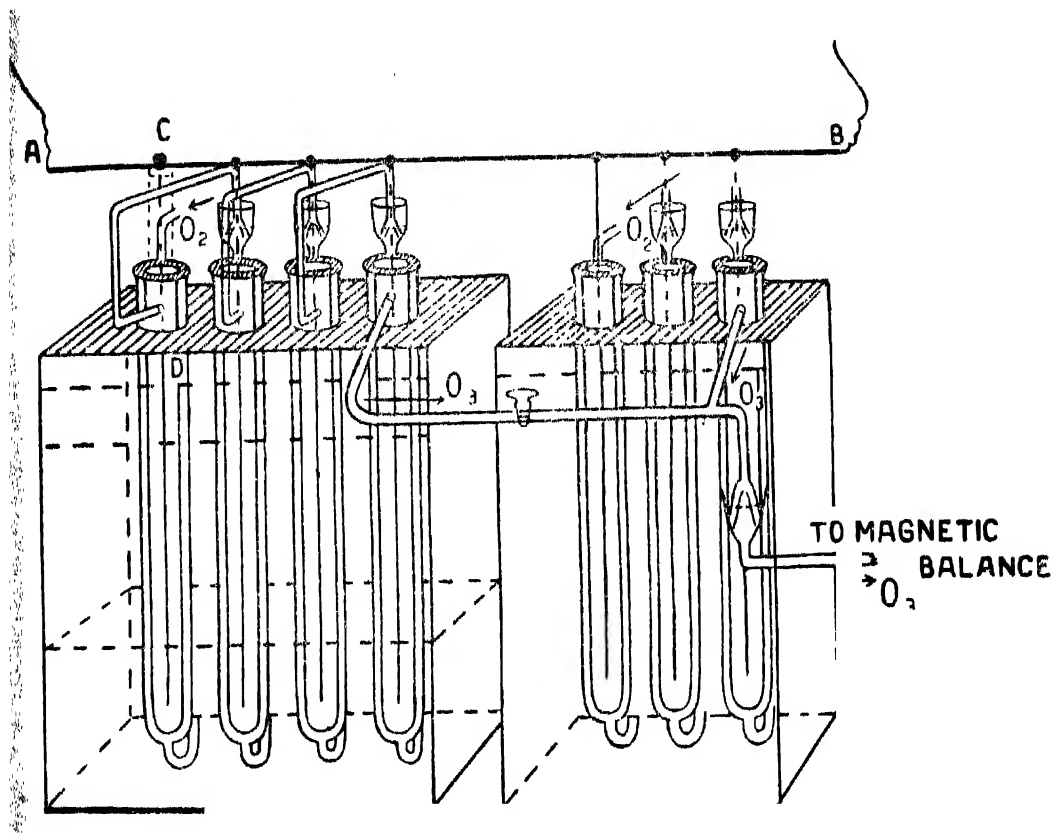
Fig. II.

The ozonising battery consists of 7 Berthelot tubes (Fig. II). The maximum yield was about 10% by weight or 7% by volume. This was constructed in the laboratory. Harries,[6] De Luserna [7] and Smith, [8] have also constructed high concentration ozonisers for their chemical investigations. The present one is constructed fairly on the model of that of

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[6]   Harries, Ann., 343, 311 (1905).

[7]   De Luserna.   Helvetica Chim Acta, 7, 62 (1924).

[8]   Smith, L. I., Jour. Amer. Chem. Soc., XLVII, 1845 (1925).

Smith, who employed 3 Berthelot tubes. As will be seen subsequently, it is not so much the high concentration as the steadiness with which the ozone battery could work and the accurate estimation of the concentration, that counts for our purpose.

Each Berthelot tube is about 40 cms. long and the diameter of the outside tube is about 42 mms. The interspace in which the oxygen is submitted to discharge is $3\frac{1}{2}$ mms. The inside tube is 35 mms. in diameter and is fused perfectly coaxial with the outer one; this fusing being exceedingly troublesome. Oxygen enters at the bottom of each tube and after partial ozonisation escapes into the second one. The connection between them is made by mercury seals and shown in the diagram. Each set is contained in a tin box enclosed in wooden cases. The cover of the box is an ebonite plate with holes into which the ozonisers, together with the side tubes carrying the inside seals, can pass through. About 8 inches from the bottom there is a similar metallic plate, so that the Berthelot tubes sit well when lowered into the box. The tubes are assembled with their "inside seals" and side tubes. The series connection between each ozoniser is then made by fusing the outside seals *in situ*. The parallel connection between the two sets is similarly made by fusing the exit tubes to a mercury seal T piece. The ozone tubes and the magnetic balance thus form an all glass apparatus.

The outside boxes $19'' \times 17'' \times 10''$ were nearly filled with water and earthed. The inside conductor was also tap water, as this is sufficiently conducting at the high voltage. A thick copper rod AB, about a metre long and held by ebonite clamps, is raised to the high potential by an interrupter and induction coil. Seven long copper wires serving as electrodes are suspended from it. These are insulated from C to D. D is the surface of water in the inner tube. Great difficulty was felt due to the high humidity of the atmosphere and conduction currents through the walls of the tube. The ebonite

plates and rods were subsequent improvements. The distance between the centres of the ozonisers were about 10 cms.

Cylinder oxygen dried and cooled by passing through a copper coil 20 metres long (kept immersed in a freezing mixture) was employed as the source of gas.

Discussion of possible errors and the magnitude of the effect sought for.

In attempting to obtain an idea of the magnetic property of ozone the following considerations have to be taken account of.

If ozone possesses an anamolous paramagnetism, a concentration of 7 to 10% is sufficient to yield a quantitative value.

If the paramagnetism is of the order of NO or ClO_2, then a 7% concentration of ozone would correspond to a change of susceptibility corresponding to about an alteration of pressure of $1\frac{1}{2}$ cms. of oxygen from that of the atmosphere. In a torsion balance where the retorsion angle corresponds to 100 minutes in oxygen, there will be a reduction of 7 minutes in the retorsion angle (when the mixture is admitted) due to the decrease in the partial pressure of oxygen and an increase of $1\frac{1}{2}$ minutes due to partial susceptibility of ozone, the total change being $5\frac{1}{2}$ minutes. If we consider the various sources of error, it is quite possible that this may appear as 5 or 7. In the latter case ozone would appear to possess no susceptibility. With great precaution, it is possible in this case to decide the sign of the susceptibility, though quantitative estimation would still be uncertain.

On the other hand if the gas is diamagnetic, assuming it to possess a susceptibility of the order of CO_2 or SO_2, then with the same balance a 7% concentration will be responsible for about $\frac{1}{20}$ mts. or 3 seconds. (The volume susceptibility of such a diamagnetic gas is only $\cdot001 \times 10^{-6}$, so that assuming a

cent % concentration of ozone, the same balance would give only $0.001/0.15 \times 100$ minutes or a 7% concentration about 3 seconds.) This demands an accurancy of 3 in 6000 seconds, the latter being due to oxygen,—an amount impossible to be detected.

The different sources of error that are involved, are may times greater than this amount, even under conditions that have been developed with great care.

The volume concentration of ozone is determined by drawing a known volume of the gas through potassium iodide solution and titrating the liberated iodine (after acidifying) by sodium thiosulphate solution. This is repeated during each experiment, since the percentage depends on the rate of passing the gas and it cannot be assumed that the concentration remains the same under the same conditions. Taking into account the various processes as the measurement of the volume of the gas, etc., an error of 1 % is quite possible in such an analysis. Thus if a 6 % concentration is analysed as 6.1 a mistake of 1mm. occurs in the estimation of the partial pressure of oxygen. This would account for about 10 seconds an amount $2\frac{1}{2}$ times that caused by ozone.

Oxygen obeys Curie's law and calculations would show that a change of $\frac{1}{10}$ degree would account for about 5 seconds.

This error can to some extent be minimised by a series of preliminary investigations, so that the influence of temperature on the suspended system compensates for that on oxygen. These could be done only approximately as the processes involved are exceedingly troublesome.

The slightest fluctuation of current was responsible for about 3 minutes, an amount 40 times due to ozone. The current was kept as constant as possible and the suspended system was changed so that the fluctuations had as little effect as possible. This and the temperature maintenance

have been sufficiently discussed in one of the previous papers.[9]

Thus it is only possible under these conditions, to examine if ozone possesses a paramagnetism comparable to that of the known gases, and by the method of statistical probability of errors, decide the sign after a series of experiments. It was with this end in view, that a number of investigations were conducted on different days and conditions.

With a view to test the accuracy of the balance, the susceptibility of air was determined. In determining the relative deflections, it is necessary to know the position of the test system corresponding to that of vacuum. It was not possible to evacuate the magnetic balance, for the metallic junction of the rotatable scale with that of the vernier, could not be made perfectly air-tight. During the rotation it invariably leaked. Thus the position in an atmosphere of pure hydrogen is taken as that corresponding to that of vacuum. Since the susceptibility of hydrogen is about $\frac{1}{800}$ of that of oxygen, this causes no appreciable error. Taking the value of oxygen at N. T. P. as $\cdot148 \times 10^{-6}$, air yielded a value of $\cdot0306 \times 10^{-6}$, closely agreeing with that of Sone.[10] This ensures that the balance is accurate and there are no bogus effects.

Results.

In the following tables, column 1 is the current; column 3 gives the temperature fluctuations during the observations; column 4, the volume per cent. of ozone; 5, the torsion head readings; 6, shift in the spot of light; (these are given only in the last experiments, since in the initial ones the shift was restored) 7, the relative retorsion angles; (the upper ones in o_2 and lower in the mixture) 8, the ratio of

[9] Vaidyanathan, V. I., *loc. cit.*

[10] T. Soné, Phil. Mag., XXXIX, p. 305 (1920).

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the susceptibility of mixture to that of oxygen; 9, the ratio of the susceptibility due to the partial pressure of oxygen to that at atmospheric pressure. The gas or the mixture was at atmospheric pressure. It may be observed that when the ratio in column 8 is less than in 9, a diamagnetic tendency is exhibited by ozone and *vice versa*. The relative retorsion angles in column 7 are also a measure of the sensitiveness of the individual experiments. Column 10 gives the sign of susceptibility as deduced from each experiment.

SERIES I.

Table I.

1	2	3	4	5	7	8	9	10
9·9 Amp	O_2	27·8		244°−45′	7°−34·2′			
			6·05	252−30·2′		·927	·939	Diamagnetic.
,,	O_3	28		244−37′	7−1·8′			
				251−38·7′				

SERIES II.

Table II.

1	2	3	4	5	7	8	9	10
0		30·7		239−46′				
5	O_2	30·5	6·05	241−57·1′	2−11·1′	·953	·940	Para.
5	O_3	30·4		2 41−51′	2−5′			
0		29·8		123−29′				
4·3	O_2	30	4·1	128−22′	4−53′	·963	·959	Para.
4·3	O_3	29·8		128−11′	4−42′			
0		28·9		96−48′				
4·3	O_2		4	92−0′	4−48′	·955	·960	Dia.
4·3	O_3	28·9		96−12·4′	4−35·6′			

SERIES III.
Table III.

1	2	3	4	5	6	7	8	9	10
0		30·3		96 — 22′	230·5				
4·3	O_2		6·1	92 — 20′	230·5	4 — 2′	·059	·939	Para.
4·3	O_3	30·3		92 — 35·5′	235·5	3 — 52·5′			
0		30·2		97 — 12′	214·5				
4·2	O_2		5·5	93 — 5′	214·5	4 — 7′	·895	·945	Dia,
4·2	O_3	30·2		93 — 27·4′	218·5	3 — 44·6′			
0		28·5		96 — 12′	210·5				
6·4	O_2		4·5	88 — 45′	211	9 — 27′	·992	·955	Para.
6·4	O_3	28·6		88 — 50′	212·5	9 — 22′			
0		29·8		91 — 47′	297				
6·4	O_2		4·9	98 — 47′	302·5	7 — 0′	·952	·951	0
6·4	O_3	29·9		99 — 7′	306.5	6 — 40′			
0		31		97 — 47′	206				
6·3	O_2		3·9	89 — 30′	206	8 — 17′	·949	·959	Dia.
6·3	O_3	31		89 — 55′	212	7 — 52′			
0		30·1		97 — 1′					
3	O_2		5·5	95 — 11′	207·5	1 — 50′	·896	·945	Dia.
3	O_3	30·2		94 — 59·4′	211·5	1 — 38·6′			
0		30·8		95 — 46′	200·5				
3	O_2		4	93 — 44′	200	2 — 2′	·971	·960	Para.
3	O_3	30·8		93 — 48·4′	201·5	1 — 58·6′			. . .
0		28·7		95 — 88′	200·7				
3	O_2		5·1	94 — 11′	203·7	1 — 47′	·889	·949	Dia.
3	O_3	28·8		94 — 22·8′	207·5	1 — 35·2′			
0		30·2		90 — 31′	252				
4	O_2		4·9	87 — 4′	252	3 — 27′	·931	·951	Dia.
4	O_2	30·2		87 — 18′	256·5	3 — 13′			

Results of a few experiments are given in the table above, to indicate the general trend of observations, others including traces of ozone, etc., having been left out.

Discussion of results.

A sufficient number of experiments have been carried out to decide with fair certainty the sign of the susceptibility of ozone gas. It could be seen from what was said above, that the errors are many times that due to the effect of ozone if it is diamagnetic. Of the various experiments carried out, in 2 cases calculations for cent. per cent. ozone yielded a paramagnetic value about $\frac{1}{2}$ and $\frac{2}{3}$ of that of oxygen. These observations were with high currents, where the steady maintenance is exceedingly difficult. When the current in the magnet was kept low and the conditions were maintained steady, there were more cases to show that ozone has a diamagnetic value or it contributes nothing.

If ozone possessed a paramagnetism, the arrangements were such as to indicate it fairly constant, for paramagnetism is generally many times stronger than diamagnetism. In polyatomic molecules a low paramagnetism may occur, but ozone is triatomic and ClO_2 has a paramagnetism of about $\frac{1}{3}$ of that of oxygen. Against this the small susceptibility of No_2[11] may also be mentioned.

In the previous investigation on ozonides,[12] ozone in combination was found to possess a distinct diamagnetism. From the number of experiments and statistical probability of errors, it seems fairly conclusive that ozone is diamagnetic in the free gas also. Traces of ozone were sufficient to show the decrease in force in the mixture, though even here, the decrease in the partial pressure of oxygen may be responsible

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[11] T. Soné. Tohoku Uni Sci Reports, 11 (3) 139 (1922).

[12] Vaidyanathan. V.I, Ind. Jour. Phys. 11 (iv) 421, (1928).

to a large extent. There was not a single case where the observations fell at the same points in pure oxygen and in the mixture, the force in the latter being distinctly less and the spot of light showing a decided shift of 2 to 5 mms. in the different experiments. Since the deduction of the susceptibility in this investigation depends on the statistical probability of errors and on the strength of our knowledge that paramagnetism is generally stronger in magnitude than diamagnetism, unless we have direct evidences to the contrary, the results may be relied on. At any rate neither an anamalous paramagnetism mentioned in literature, nor a paramagnetism of the order that is generally known to exist in gases, is present in ozone. There is an overwhelming evidence from the experiment that it is diamagnetic.

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On the Diamagnetism and Structure of Ethylene

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ABSTRACT.

By the torsional method previously employed by the author in the study of the relation between diamagnetism in the liquid and vapour states,[1] the magnetic susceptibility of ethylene (which was supposed to be paramagnetic according to Lewis[2] and Quincke[3]) was studied. The gas was found to be diamagnetic with a value of $15\cdot3 \times 10^6$ for the molecular susceptibility. This value is in fair accord with Pascal's law

$$\chi_m = \Sigma\chi_a + \lambda$$

The value is also equal to that of sulphur having the same number of electrons. The structure of the molecule is discussed from the magnetic and chemical standpoints.

Introduction.

According to Quincke's[4] investigation, ethylene is a feebly paramagnetic gas. From considerations of unsaturation and chemical analogy with oxygen, Lewis assumed that each atom in the molecule of ethylene is an odd atom and possesses a magnetic moment. Pascal's[5] investigation led

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[1] Vaidyanathan, V. I., Ind. Jour. Phys., Vol. II, Part II, p. 135.

[2] Valence and Structure of Atoms and Molecules (Chemical Catalog Co., p. 89).

[3] Quincke, L.B. Tables.

[4] Quincke, *loc. cit.*

[5] Pascal, P. Magnetochemie, Wedekind. p. 94 (1911).

him to the conclusion that the ethylene bond has a para-magnetic value of 5.7×10^{-6}. The gas does not seem to have been investigated after Quincke. Being a typical un-saturated compound, it is of extreme importance to possess an accurate knowledge of its magnetic property. The follow-ing investigation is accordingly undertaken.

Experimental Arrangements.

These are essentially the same as that described in one of the previous communications "On the Relation of Dia-magnetic Susceptibility in the Liquid and Vapour States"[1] ; necessary improvements in the technique having been effected. A test system consisting of three tubes, is attached together and made astatic, so that there is very little force acting on it, when surrounded by a magnetic field in vacuum. This is surrounded in turn, by a standard gas and the gas in question. It is known that the volume susceptibilities are proportional to the relative retorsion (or torsion if it is small) angles. Constancy of temperature, current, etc., have been discussed in the paper "On the Relation of Diamagnet-ism in the Liquid and Vapour States."

The apparatus was all glass and the gas was not allowed to come in contact with rubber. The thermometer employed, enabled $\frac{1}{20}$°C to be read and this was fused to a side tube.

The gas was prepared from sulphuric acid and ethyl alcohol. This was purified for freeing from the higher homologues, sulphur dioxide, etc. Because of the many purifying trays, the collecting vessel could not be evacuated. Hence to avoid traces of air, which vitiate the results con-siderably, carbon dioxide was passed by an auxiliary tube, connected to the preparation flask, for about 10 hours, after which it showed diamagnetism. Ethylene was then passed

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[1] Vaidyanathan, V. I., *loc. cit.*

through the apparatus for about 5 hours, replacing the carbon dioxide in the collecting jar.

The volume susceptibility of ethylene is compared with that of dry air, the value of air being taken as 0.0308×10^{-6} at 0 and 760.[1] The torsions were directly read, as these were small. In the case of air a calibration curve was obtained and the value for ethylene computed from known deflections.

RESULTS.

Temperature.	P. in mms.	Deflections.	Temp. Correction.	Relative torsion angle.	Deflection per mm.
32·5	0	180	...	...	...
32·55	630	192·5	+ 1	13·5	·021
32·3	630	189	...	...	...
32·5	1	174·5	− 1	14·5	·023
32·2	0	164	...	...	...
33·25	510	174	1	11	·021
33·25	510	174	..	.	...
33·25	0	162·5	0	11·5	·022
				Mean	·0218

A calibration curve over the same region yields 0·87 divisions per mm. change of pressure of air at 34·5°C. Making the necessary calculations for temperature effect on air according to Curie's law, this gives a change of volume susceptibility of 0.0000367×10^{-6} per division on the scale. Over the same region, 1 mm. change of pressure of ethylene causes 0·0218 divisions; taking the mean temperature of observations as 33°C. Thus the volume susceptibility of

[1] Taka Sone, Phil. Mag., XXXIX, p. 305 (1920).

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ethylene at 0 and 760, is—0.000681×10^{-6}. Multiplying this by the molar volume, the molecular diamagnetic susceptibility comes out as 15.3×10^{-6}.

Additive Law and the Diamagnetism of Ethylene.

According to Pascal's [1] additive law, the double bond exerts a paramagnetic value, 5.7×10^{-6}. If then we assume the same value for the bond in ethylene, the diamagnetic susceptibility of the gas can be approximately calculated. According to Pascal, the atomic susceptibility of carbon is —6×10^{-6} and hydrogen—2.95×10^{-6}. Thus C_2H_4 has a value—23.8×10^{-6}. If the paramagnetic contribution of the link is taken account of, the diamagnetic susceptibility is —18.1×10^{-6}. The observed value is—15.3×10^{-6}, a sufficiently close approximation, considering the experimental difficulties and the approximate nature of the additive law in unsaturated compounds.

It has been suggested by Stoner,[2] that in the ethylene bond the carbon and hydrogen nuclei are partly inside a closed electronic configuration. The decrease in diamagnetic susceptibility is then accounted for, by the contraction of the outer orbits. A highly contracted outer shell is not suggested by the viscosity data which gives $\frac{\sigma}{2}$ as 2.72A.

Although quantitative considerations are beset with difficulties, a closed configuration approximating to that of atoms is also suggested by the fact that sulphur with 16 electrons has the same susceptibility as ethylene, which has also 16. The specific susceptibility of sulphur is —0.48×10^{-6} according to Honda.[3] Hence the atomic susceptibility is —15.4×10^{-6}. This is also constant between 18 to 300°C.

[1] Pascal, loc. cit.

[2] Stoner, E. C., Magnetism and Atomic Structure, p. 332.

[3] Honda and Owen, Annalen der Physik, 37, 675 (1912).

Regularity in the Susceptibility of Molecular and Atomic Configurations.

It has been previously suggested that nitrogen has also a closed configuration with the 2 nuclei and the K electrons inside a common configuration.[1]   The magnetic, spectroscopic and chemical properties point to the validity of such a conception in many cases, though sometimes the ground terms expected from the analysis of the band spectra data, do not coincide with the suggestion of the magnetic investigations.

If we examine the magnetic data of nitrogen, sulphur, ethylene and argon, a beautiful gradation of magnetic property is discovered.   In the case of atoms of similar configurations, a linearity of atomic susceptibility and number is found to exist as in the case of alkali metals. [2]   Rubidium however shows a divergence.   Joos [3] has shown a linear relation in ions of chlorine, bromine, iodine, etc.

It may now be pointed out that in molecules as well, with a closed configuration, a similar linearity exists.

TABLE II.

	N_2	S	C_2H_4	A
No. of electrons	14	16	16	18
Molar or Atomic Sus. ...	12·4	15·4	15·3	$19·05 \times 10^{-6}$

In the above table the value for nitrogen, is the mean between the author's [4] and Hector's [5] value, and for argon the mean of Lehrer's [6] and Hector's value, as these are very near

[1] Stoner, E. C., Phil. Mag., III, 336 (1927).

[2] Mc Lennan, J. C., Ruedy (R.) and Cohen, E. R., Proc. Roy. Soc., 118, 468 (1927).

[3] Joos George, Zeit. f. Phys. 2, 201 (1920).

[4] Vaidyanathan, V. I., Phil. Mag., V, 380 (1928).

[5] Hector, Phys. Rev. 24, 418 (1926).

[6] Lehrer, Ann. der Phys., XXXI, 229 (1926).

and the mean may not be far from the truth. These are plotted in the graph.
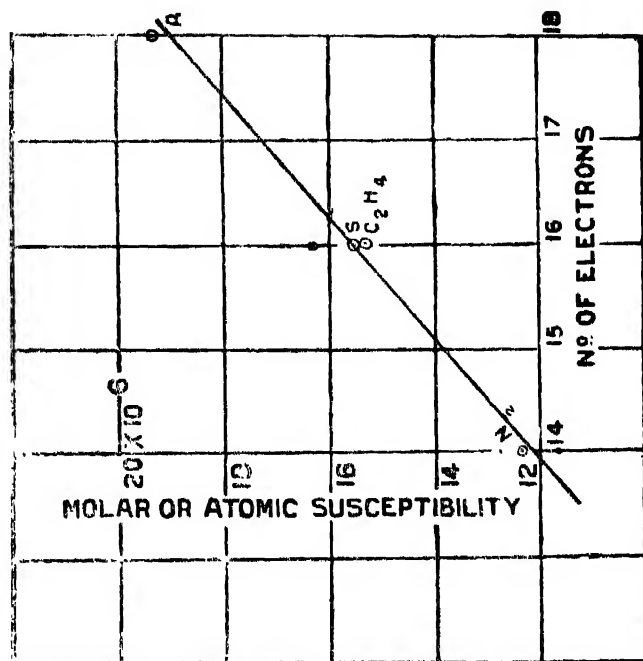
The general nature of the curve is noteworthy, for the accuracy of the magnetic data does not permit of a very exact verification of the linearity, but within experimental errors, the graph is nearly a straight line. (The small dots in the graph are also the different values.)

If we accept nitrogen as a standard of molecular stability just as argon is one of atomic, the formation of the additive compounds of ethylene such as ethylene chloride, can be explained as follows. The two valency electrons of the ethylene molecule may be assumed to have been transferred to each chlorine atom, striving to form a stable configuration of argon. The ethylene molecule then has 14 electrons which adjust to form a stable molecular configuration. The configuration inside the common shell is much more complicated than in nitrogen, for there are as many as 6 nuclei with their K electrons and a crude model can be suggested only

with diffidence.   It is also interesting to observe that these compounds are generally polar. [1]

On the Structure of Ethylene.

The usual method of representing the possible structures of ethylene is

$$(1) \quad H : \overset{H}{\underset{\cdot}{C}} : \overset{H}{\underset{\cdot}{C}} : H \quad (2) \; H : \overset{H}{\ddot{C}} : \ddot{C} : H \quad (3) \; H : \overset{H}{\ddot{C}} : : \overset{H}{\ddot{C}} : H \quad (: \ddot{O} : \ddot{O} :)$$
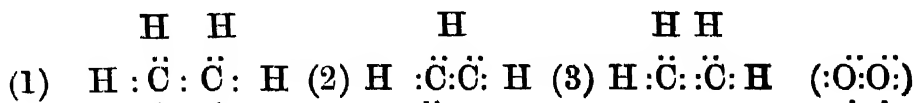
According to Lewis [2] though the molecule of ethylene is even, each atom is considered odd, and the chemical analogy with oxygen points to the conclusion that structure (1) is the most probable.   Like the oxygen molecule, ethylene was then supposed to possess a magnetic moment, quite unlike other organic compounds.   Lewis also mentions, however, that none of these structures are adequate to represent completely the behaviour of ethylene.   At any rate, the present investigation definitely shows that ethylene has no magnetic moment; and the analogy with oxygen is not necessary.   Further, the magnetic data suggest a strong analogy with sulphur.

Structure (2) is the least probable as was shown by Smyth,[3] for this would possess a very strong electric moment, whereas ethylene has no measurable moment.

Structure (3) is the only possible one that is admissible, consistent with the magnetic and electric moment data.

Even here, the representation does not seem to agree with the picture afforded by the magnetic analogy. A closed configuration as in the case of nitrogen with the nuclei inside, (the K electron orbits are not seriously influenced) is what the linear relation and equality with the magnetic property of sulphur suggest.

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[1] Smyth, C. P., Journal of the American Chemical Society, XLVI, 10, 2151 (1924).

[2] Valence and Structure of Atoms and Molecules (Chemical Catalog Co., 1924, p. 89. 124).

[3] Smyth, C. P., Journal of the American Chemical Society, 42, 2503, (1925).

Assuming an atom-like configuration; we shall now make a rough calculation of the order of molecular radius and compare it with those obtained in the case of atoms from susceptibility data and viscosity.

If the hydrogen is inside the electronic configuration and near the carbon nucleus with the K shell, we may reasonably assume the orbits in hydrogen to be distorted, because of the small nuclear charge in hydrogen and larger radius of the orbit. The paramagnetic contribution of the ethylenic bond which according to Pascal is 5.7×10^{-6} may then be attributed to the complicated core rather than to the outer orbits. Since hydrogen has a susceptibility -2.95×10^{-6} according to Pascal and there are 4 of them in ethylene, this will give—taking into account the bond value—to the outer orbits a susceptibility of -9.8×10^{-6}. The two carbon nuclei with the K orbit contribute very little. Thus, of the 16 electrons, only 4 are free to rotate in large orbits, as the others are bound inside the shell.

Applying the usual formula

$$r^2 = -\frac{6mc^2}{N n e^2} \chi_A$$

where n is now 4 and χ is 9.8×10^{-6} we obtain $.93$A. as the mean radius of the outer orbit. The susceptibility 15.3×10^{-6} for ethylene, also suggests that the outer orbits are in a shell somewhat similar to the M shell in the argon atom.

The radii of the orbits may now be compared.

	Magnetism	Viscosity
Argon	$.83$ A	$1.83, 1.42$ A [1]
Ethylene	$.93$ A	2.7 A.

If for orbits characterised by the same quantum numbers $r \propto \frac{1}{Z^2}$ where Z is the effective nuclear charge, then the radius of the outer orbits in ethylene is still larger than the one calculated above. This indicates that of the 4, the two

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[1] For viscosity data see Jean's Dynamical Theory of Gases.

valency electrons move in orbits larger than that of the M shell in argon, probably in orbits corresponding to that of an atomic N shell. (The extact calculation is not of much value, because of the uncertainty of the effective charge and the presence of the various nuclei inside the common shell.)

If they are moving in such large orbits, the mobility of the double bond, the formation of additive compounds and the large radius of the molecule (according to viscosity considerations) follow naturally.

It is also interesting in this connection to observe that carbon monoxide and nitrogen, having the same number of electrons and magnetic property, possess the same radii according to viscosity also. The radii being 1·88 and 1·89 A. The radii according to viscosity considerations, are always larger than those of diamagnetism and this is because of the different considerations of the problem. What is only meant to show in the foregoing, is the order of magnitude and nearly the same ratio for closed configurations.

Considering the electronic sublevels in a molecule, Birge points out "that the energy levels associated with the valence electrons in molecules agree in all essential aspects with those associated in valence electrons in atoms." (Birge, R. T., Nature, CXVII, 300, 1926). This has been applied to simple binuclear systems and even here the analogy is not quite complete. As such it is of little use to attempt to attribute any atom-like sublevel to the valency electron in ethylene. Further the diamagnetic data taken alone, do not enable us to fix this. With the analysis of the band spectrum and the magnetic data, it may be possible to fix the corresponding atom-like sublevel in such a configuration.

As the foregoing considerations show, it does not appear to be far in the wrong, to seek molecular stability and

configuration, along the line of building up of atoms, with slight modifications.

I have great pleasure in thanking Prof. C. V. Raman, F. R. S., under whose kind suggestion and guidance the work was carried out. These were conducted in the Laboratory of the Indian Association for the Cultivation of Science.

210, BOWBAZAR STREET,
    CALCUTTA.

15

Photographs of Coronas in Monochromatic Light

BY

BY

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Presidency College, Calcutta.

(Plates VI, VII and VIII.)

(*Received for publication, 5th August, 1928.*)

Abstract.

Many investigations have recently been made on the theory of coronas produced by water droplets, and on their experimental observation. References to the recent literature are given in the paper. But so far as the writer is aware, no photographs of such coronas in truly monochromatic light have been published. In the present investigation a series of photographs have been taken with water droplets of uniform size of the coronas observed with 4358 A.U. radiations of the quartz mercury arc. The photographs are arranged in order of increasing size of the water droplet and are reproduced with the paper. They show that the positions and distributions of intensity of the rings in the coronas *as observed in truly monochromatic light,* differ very widely from the simple type of Fraunhofer diffraction pattern due to an opaque spherical obstacle. The changes in the coronas with change of the ratio between size and wave length are very rapid.

1.   *Historical Survey.*

Coronas consist of one or more sets of rainbow-coloured rings, usually of only a few degrees radius, concentrically surrounding the sun, the moon, or other bright object when covered by a thin veil of cloud. They differ from halos in

4

having (except in rare cases) smaller and variable radii and in having the reverse order of colours; that is blue nearest the sun, say, and the red farthest away.

Clearly then, the coronas are caused by the diffraction of sunlight by the droplets of water suspended in the atmosphere. The parallel beam of sunlight falls on the layer of innumerable droplets of water and undergoes diffraction. The droplets, on account of their very short focal lengths and consequent dispersive power, affect the parallel beam substantially in the same way as would so many opaque discs, each of the size of a great circle of the corresponding droplet and normal to the line of travel. Futhermore, as the incident light is parallel, the centres of the droplets may be regarded as lying in a common plane, each being located where the line of sight to its actual position intersects the plane in question. The problem then reduces to that of finding the diffraction pattern produced in an isotropic transparent medium by a great many irregularly distributed opaque discs on a plane wave front of monochromatic light. The problem can be handled with the aid of the well known Babinet's principle.

Fraunhofer found that the phenomenon of coronas is analogous to the diffraction phenomenon with little circular opaque discs and that it can be imitated when a bright source of light is viewed through a glass plate sprinkled with lycopodium podwer. In white light, the diffraction phenomenon with little circular discs consists of the direct visible source of light, in the middle, with a bluish white coloured central field surrounded by brownish red circles followed by a dark violet ring and alternate green and red rings. In monochromatic light, they consist of dark and bright rings of decreasing intensities surrounding concentrically the source of light. The rings obey the law $Z = \dfrac{r}{\lambda} \sin \theta$ where θ is the angle of diffraction, λ, the wave length of light, r, the radius

Fig. I

Fig. II

Fig. III

Fig IV

Photographs of Coronas

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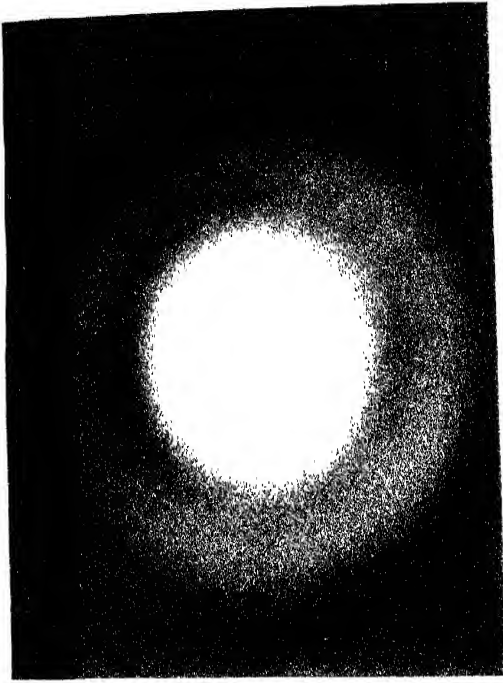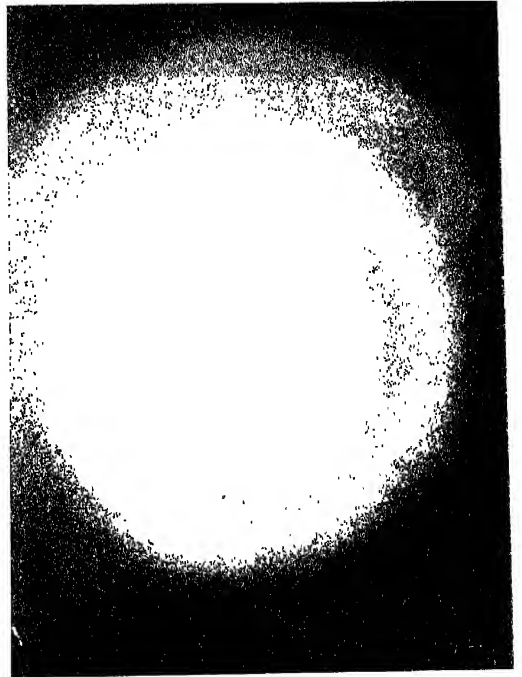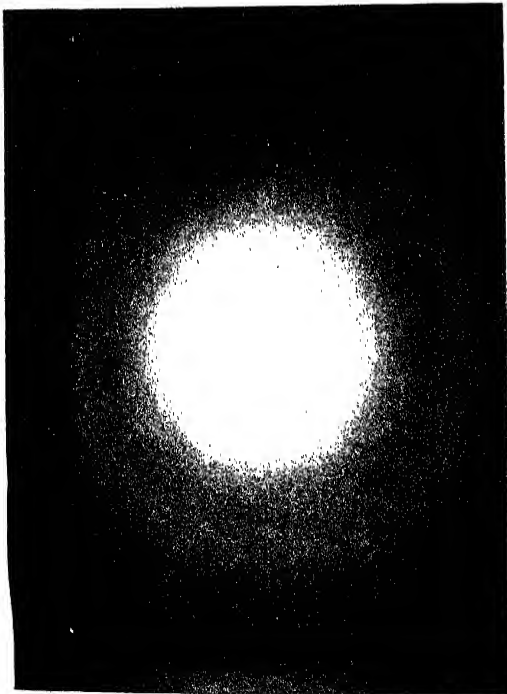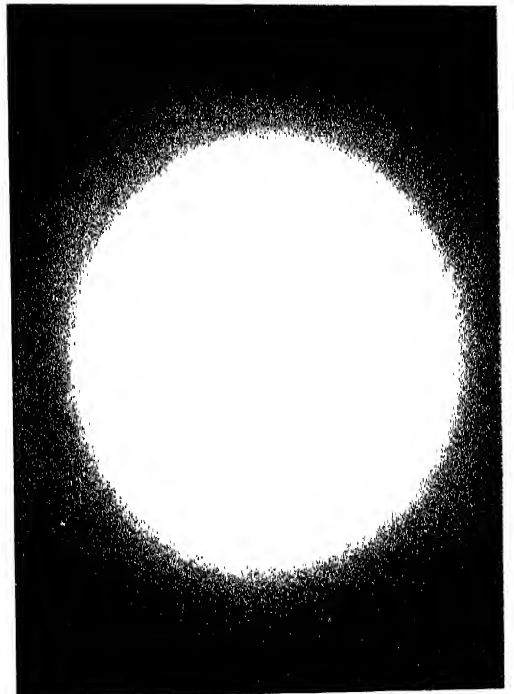
of the droplet and Z is constant and is equal to 0·61 for first dark ring and 1·116 for the second dark ring. The radii of the drops can be calculated from the diameters of the minima of different orders.

Mecke[1] imitated the phenomena of coronas in artificial mist. He took several round bottomed flasks which were put in communication with one another by means of glass tubes passing through holes perforated in the rubber corks fitted in the necks of the flasks. One of the flasks contained some water in which the artificial mist was produced, the other was connected to a manometer to note the changes of pressure inside the flask and the third one to a water pump to exhaust the air from inside the flasks. By regulating the exhaustion of the air with the water pump, clouds containing particles of any size could be obtained. It was found that with the larger homogeneous droplets, the diffraction phenomenon consisted of a white central field with a slight reddish brown edge and surrounded by the usual system of coloured rings. They are in agreement with the coronas observed round the sun and the moon, and also in agreement with the diffraction pattern produced in the experiment with the circular little opaque discs; but with smaller droplets a new phenomenon appeared. The central field, which was originally white became intensely coloured, and there was a deviation in the succession of colours in the rings, and no definite law could be established regarding the succession of colours. In monochromatic light the diffraction phenomenon showed an arrangement of maxima and minima which possessed distinctly periodical character. A calculation of the magnitudes of the drops from the diameter of the rings was not possible. The deviation decreases with the growth of the size of the droplets and the diffraction pattern approaches the normal one.

[1]   R. Mecke, Ann. d. Phys., Vols. 61, 62, 63.

To account for the anomalous diffraction pattern in the case of the small droplets, Mecke introduced a complicated formula instead of the simple diffraction formula for circular little opaque discs. As the droplets are transparent, it was assumed that the light passing through the drops and that reflected at the surface of the drops interfered with the diffracted beam, but the magnitude of the drops could not be calculated from the measurement of the diameter of the rings. As for larger droplets, as they occur in the experiment or in nature, the old formula for the calculation of the radius of the drops from the diameter of the rings is used. The influence of the transparency of the drops and the reflection over the surface do not then come into consideration. The larger particles behave as opaque circular discs. Ray[1] observed that Mecke's derivation of formula being based on elementary methods could not be strictly applied. Accordingly he treated the problem strictly from the Electro-Magnetic Theory of Light. He made use of the Rayleigh[2] expression for the scattered wave, $\dfrac{Z - X}{r}$ representing the horizontal component and Y the vertical one where X, Y and Z denote the electrical forces parallel to the three axes in the scattered wave and r, the distance from the centre of the spherical obstacle. He concluded that the elementary theory of coronas was considerably at fault in the case of the very small droplets. Numerical values for the positions of maxima and minima calculated from the ordinary theory differ by five or six degrees from those calculated from the rigorous electro-magnetic theory which also explains the alternations in the state of polarisations in different directions of the scattered lights.

[1]   B. B. Ray, Pro. Ind. Assoc. Cult Sci., Vol. VIII, p 23 (1925).
[2]   L. Rayleigh, Proc. Roy. Soc., Vol. 84 A (1910).
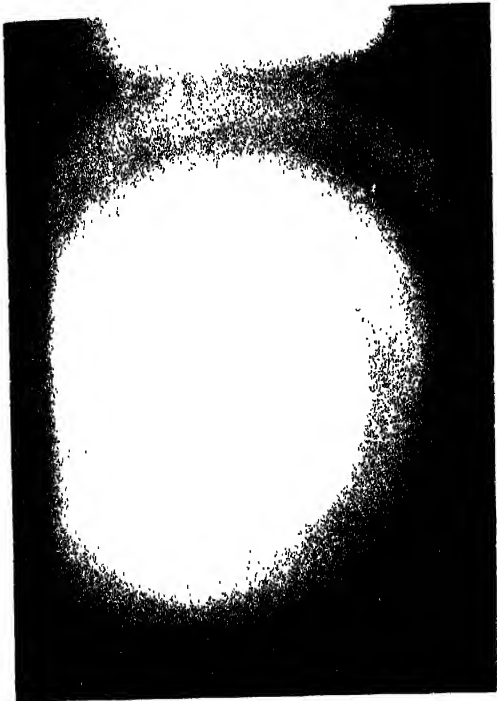
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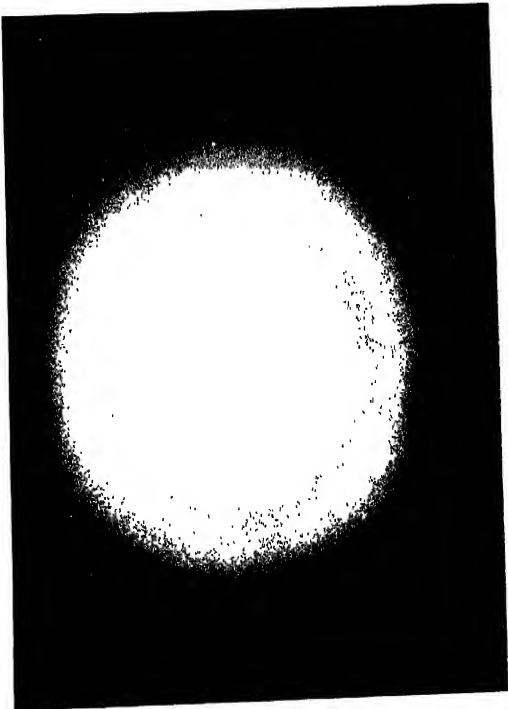
Fig. VI
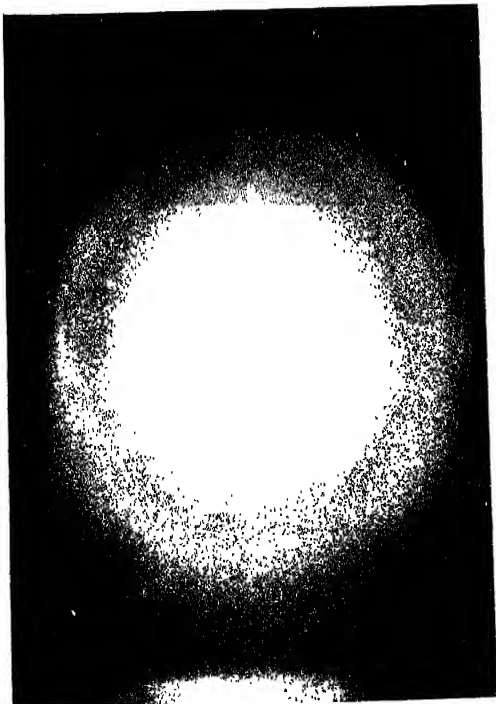
Fig. VII
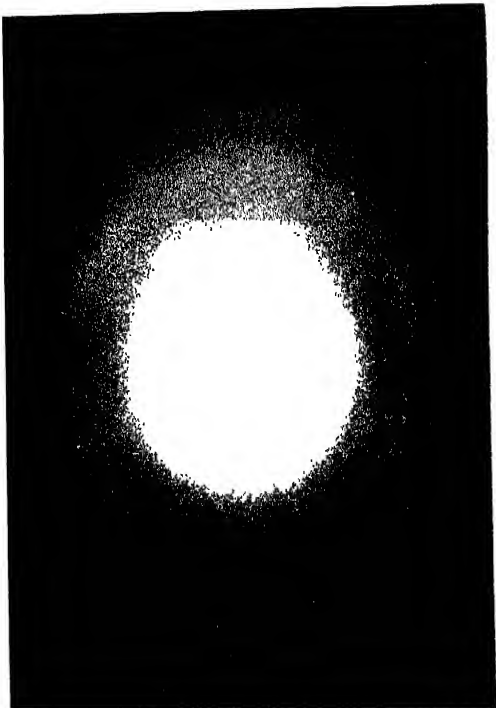
Fig. VIII

Blumer [1] found that the intensities scattered in different directions by sphere of different sizes and of different refractive indices varying from a small value to infinity with the help of the formulæ of Mie [2] given by the equation

$$J_1 = \frac{\lambda^2}{4\pi^2 r^2} \, i_1 \text{ and } J_2 = \frac{\lambda^2}{4\pi^2 r^2} \, i_2$$

where i_1 and i_2 represent the intensities of light parallel and perpendicular to the vision-plane of polarised light, λ, the wave length of light used and r, the distance from the centre of the droplets. Mie's formula is analogous to that of Rayleigh except that it is expressed in polar co-ordinates and that it is to be divided by the Rayleigh mass-factor, c—·996049. He also made a survey of all the important old and new works on the scattering of light by a small sphere and calculated the intensities both according to the pure diffraction theory and the theory of reflection and refraction and the exact electro-magnetic theory. He also came to the conclusion that in order to get a correct distribution of intensities, an additional factor depending on the scattering angle and the size of the spheres was to be taken into account and to be added to the result obtained from the bare consideration of reflection, refraction and diffraction. He also calculated the intensities of light scattered by spheres of refractive index 1·25 for different diameters from 50 $\mu\mu$, 1000 $\mu\mu$ to obtain a theoretically correct colour structure. These calculations serve to explain the colouration of a colloidal solution and of twilight phenomenon and the colour effect produced by particles suspended in the atmosphere.

2.   *Method of Photographing Coronas.*

The experimental arrangement consists of a round bottomed flask having a diameter of 24 c. m. and containing distilled water. The bottom of the flask is blackened a little, to make

[1]   H. Blumer, Zs. f. Phys., Vols. 38, 39 (1926).
[2]   G. Mie, Ann. d. Phys., Vol. 25 (1908).

the clouds as they will be formed inside the flask by the sudden expansion of water, distinctly visible against the black background. The flask is connected with two stopcocks, one connecting with a vacuum chamber and the other opening to the atmospheric air. By momentarily opening the stopcock connecting the vacuum chamber with the condensation flask, clouds are formed within the flask by the adiabatic expansion of the air saturated with water vapour. By carefully regulating the stopcock attached to the vacuum chamber, and varying the pressure inside the condensation chamber, clouds containing particles of any desired size could be obtained. As the source of light, a quartz mercury vapour lamp is used. It is surrounded on all sides by black cloth mounted on a wooden frame. In front of the frame there is a circular aperture in which a condenser fits. The rays from the mercury arc after passing through a cell containing quinine sulphate solution and a Wratten blue filter are made to converge on a circular aperture. In front of the circular aperture and at a distance of a meter and a half from it the condensation flask is placed. Behind the flask is placed the camera for photographing the coronas as they are formed. When the vapour condenses, and the mercury arc as described above is viewed directly through the condensation flask, a system of concentric bright and dark rings encircling the aperture in the middle becomes visible. The arrangement of the system of rings depends on the sizes of the droplets formed. If the sizes of the droplets are made to alter by varying the change of pressure within the condensation flask there is a rapid alteration in the arrangement of the bright and dark rings. Sometimes the second bright ring vanishes and its place is taken by a dark ring. Sometimes the third disappears and the second reappears and so on. The whole system seems to oscillate as it were. Several photographs are taken at different stages and are reproduced with the paper. The changes in the distribution of rings will be clear from the photographs.

PLATE VIII

MITRA

Fig. IX

Fig. X

Fig. XI

Fig. XII

16

Electric Moment and its relation to Chemical Constitution.

BY

P. C. MAHANTI, M.Sc., AND D. N SEN GUPTA, M.Sc.

ABSTRACT.

The paper deals with the determination of the permanent dipole moments and polarisability of the organic halides CH_3I, C_2H_5Br and C_2H_5I by the heterodyne beat method. It is found that $\mu = 1\cdot31 \times 10^{-18}$ e. s. u. for CH_3I, $\mu = 1\cdot78 \times 10^{-18}$ for C_2H_5Br and $\mu = 1\cdot62 \times 10^{-18}$ for C_2H_5I; their polarisability however is $\cdot005761$, $\cdot002300$ and $\cdot007839$ respectively. Thus it is noted that the organic halides as CH_3Cl, CH_3I and C_2H_5Cl, C_2H_5Br and C_2H_5I, has gradually weakening dipole moment with increasing atomic weight of the halogens. It is further suggested that the permanent dipole moment in compounds of this type is due to the deformation of the electron orbits of carbon and halogen which give rise to the permanent moment of the molecule. It is also suggested that the polarisability of the molecule itself due to applied field increases with the increasing atomic weight of the halogen due to the weakening of the bond of the shared electron.

Introduction.

The connection between dielectric constant and molecular structure was to some extent perceived by Faraday, but the theory has been developed by Lorentz,[1] Debye,[2] J. J. Thomson,[3] Gans[4] and Pauli.[5]

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[2] P. Debye, Phys. Zeit., 13, 97 (1912).

[3] J. J. Thomson, Phil. Mag., 27, 757 (1914).

[4] Gans, Ann. d. Physik, 646, 481 (1921).

[5] Pauli, Zeit. fur Physik, 6, 319 (1921).

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The paper deals with the determination of the permanent dipole moments and polarisability of the organic halides CH_3I, C_2H_5Br and C_2H_5I by the heterodyne beat method. It is found that $\mu = 1\cdot31 \times 10^{-18}$ e. s. u. for CH_3I, $\mu = 1\cdot78 \times 10^{-18}$ for C_2H_5Br and $\mu = 1\cdot62 \times 10^{-18}$ for C_2H_5I; their polarisability however is $\cdot005761$, $\cdot002200$ and $\cdot007839$ respectively. Thus it is noted that the organic halides as CH_3Cl, CH_3I and C_2H_5Cl, C_2H_5Br and C_2H_5I, has gradually weakening dipole moment with increasing atomic weight of the halogens. It is further suggested that the permanent dipole moment in compounds of this type is due to the deformation of the electron orbits of carbon and halogen which give rise to the permanent moment of the molecule. It is also suggested that the polarisability of the molecule itself due to applied field increases with the increasing atomic weight of the halogen due to the weakening of the bond of the shared electron.

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[5]   Pauli, Zeit. fur Physik, 6, 319 (1921).

As a result of an enquiry into the cause of the variation of dielectric constant of substances in the gaseous state Debye postulated that these molecules have permanent electric dipoles contributing to their polarisation in an electric field. Assuming farther that the molecules are under the influence of an isotropic polarisation field and the molecular orientation is affected by temperature according to the well-known Maxwell-Boltzmann distribution law, Debye worked out the following relation

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = 4\pi N \left(\gamma' + \frac{\mu^2}{3KT} \right) \qquad \dots \ (1)$$

where ϵ is the dielectric constant, M the molecular weight, ρ the density at the temperature T, N the Avogadro number, K the Boltzmann gas constant, and γ^1 a constant depending on the polarisability of the substance and μ the permanent moment of the dipole in the molecule.

Assuming that the vapour obeys perfect gas laws, we have

$$\frac{1}{\rho} = \frac{P_0}{P\rho_0} \cdot \frac{T}{T_0},$$

Thus

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{MP_0 T^2}{P\rho_0 T_0} = \frac{4\pi NT}{3} \left(\gamma^1 + \frac{\mu^2}{3KT} \right) \qquad \dots \ (2)$$

Taking

$$\epsilon + 2 = 3$$

$$\frac{(\epsilon - 1)}{3} \cdot \frac{P_0 T^2}{P} \quad \frac{4\pi N P_0 T_0}{3M} \left(\gamma^1 T + \frac{\mu^2}{3K} \right) \qquad \dots \ (3)$$

$$= AT + B,$$

where

$$A = \frac{4\pi N \rho_0 T_0 \gamma^1}{M}$$

$$B = \frac{4\pi N \rho_0 T_0 \mu^2}{3MK}$$

$$= \frac{4\pi N T_0 \mu^2}{K} \cdot \frac{1}{22 \cdot 4 \times 10^3}$$

Here A is a constant which represents the factor due to electric polarisation due to impressed field on the molecule and B is a constant which represents the orientation polarisation and proportional to the square of the permanent electric moment of the molecule.

The equation (3) shows that if the values of $\frac{(\epsilon-1)P_0 T^2}{\mu}$ be plotted against T, there should be obtained a straight line of slope A and intercept B. For gases and vapours of symmetrical structure, B=0, the straight line should pass through the origin of co-ordinates.

Taking molecules having symmetrical configuration of atoms, it can be easily conceived that they would not develop any permanent dipoles in them. Thus all homopolar molecules as H_2, N_2, O_2 would be free from dipoles. Zahn[6] also showed that the molecules C_2H_2, C_2H_4, C_2H_6 indicate no permanent dipole moment inspite of the unsaturated carbon bonds present in them. Sänger[7] also showed that CH_4 and CCl_4 molecules are free from a permanent moment but as the H-atoms are replaced by Cl, the molecule at once shows the assymmetry developed in it which is found to be the greatest when a single atom of H is replaced by Cl and the moment gradually diminishes as more and more heavy atoms of Cl take the place of the lighter atoms of H.

[6]   C. T. Zahn, Am. Chem. Soc. J., 47, 2501 (1925).
[7]   R. Sanger, Phys. Zeits., 27, 556 (1926).

The object of this investigation is to study the change in the constitution of the symmetrical molecules of the type of methane and ethane by replacing one of the hydrogen atoms by the different halogen atoms as revealed by the magnitude of the permanent dipole developed in the molecule.

Measuring Circuits.

The method used in setting up the circuits is in its main features similar to that used by Pungs and Preuner,[8] J. Herweg[9] and Zahn.[10] It is the heterodyne null method in which the two triode valve oscillating circuits were of frequency $1\cdot5 \times 10^6$ and $1\cdot51024 \times 10^6$. The beat frequency of 1024 in unison with a 1024 tuning fork maintained by means of another triode valve after the method of Eckardt.[11] Phillips B403 valve was used for this purpose and was found to operate very satisfactorily during the course of the work.

The relation between the variation of capacity and the frequency is clearly indicated by the equation

$$\frac{\partial n}{\partial c} = \frac{1}{2}\left(\frac{c}{2\pi\sqrt{L}}\right)\frac{1}{C\sqrt{C}},$$

and it is thus evident that the arrangement will be more and more sensitive with higher oscillation frequency of the generating circuits, but with the higher frequency the oscillators are also susceptible to the slightest change in their own circuit conditions. After trying several higher frequencies the above-mentioned one was maintained throughout the experiment. It is also well-known that the change of the beat tone with the capacity variation is smaller at lower frequencies and it is only when the beat tone is kept at a high value that the

* Pungs and Preuner. Phys. Zeit., 20, 543. 1919.

" J Herweg. Zeit. f. Physik, 3, 36 (1920).

10 C. T. Zahn, Phy. Rev., 23, 345 (1924).

11 Eckardt, J. O. S. A. and R. S., I., 6, 949 (1922).

proportionality is constant.   In our case the constant value is attained near about 1000.

A diagram of the electric circuits is shown in Figure 1.
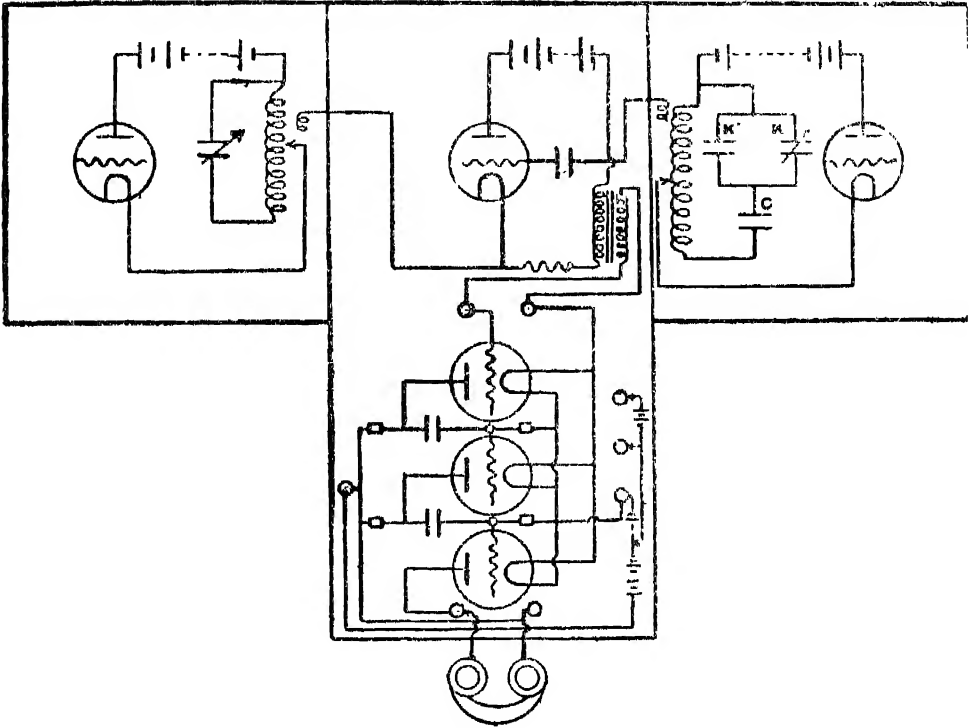
Fig. 1

The two triode generators are coupled electromagnetically to a detector amplifier circuit.   The detector amplifier circuit consists of an amplifier electron tube circuit and a Telefunken Arcolette set.

The various parts of the electrical apparatus were carefully shielded by means of earthed zinc sheet.   The two generators and the detector amplifier circuits are separately enclosed in metal boxes ; all the variable condensers are operated by insulated shafts running through the shielding boxes.

The oscillator tubes are Telefunken R. E. 144 valves operating at 100 volts on   the plate and about 4 volts on the filament.   The amplifier tube is Telefunken R. E. 073d valve

operating at 15 volts on the plates and about 3 volts on the filament. All connections were made of solid copper rods and glazite wires. Owing to the special characteristic of the valve used, no grid bias was necessary ; one possible source of error was thus avoided. The valve characteristic under operating conditions was very straight, except just at the ends and the harmonics could not be detected in the telephone used for the beat measurements. In any case, the presence of harmonics can have little effect on the results.

The system of condensers used in the variable generator consists of the three condensers K, K′ and C as shown in Figure 1. K′ is a Dubilier mica condenser type 620, of about 5000 μF. The condenser K is a precision condenser of the Bureau of Standards pattern variable air condenser manufactured by Leeds and Northrup. A certificate of standardisation indicates the values of the capacity corresponding to the divisions marked on the dial. A slow adjustment screw permits the reading of the capacity within $0.05\mu\mu$F and the values are accurate to within $\pm 1\mu\mu$F. The maximum capacity of the condenser is $1134\mu\mu$F.

The capacity (K+K′) is connected in series with the experimental gas condenser. By the use of zero-beats as a criterion of adjustment, the total capacity of this combination is always kept constant and it thus prevents also any errors arising out of the change of capacity due to frequency. It has been pointed out by Zahn that the change $\triangle C$ in the capacity of the experimental condenser due to the influx of the gas compensated by a variation of the capacity $\triangle K$ of the standard condenser is such that the differential coefficient $\frac{dK}{dC}$ is a linear function of K. An average value of $\frac{dK}{dC}$ can be used for finite values of $\triangle C$ and $\triangle K$, and then

$$\triangle C = -\left\{\frac{C}{K+\tfrac{1}{2}\triangle K+K^{1}}\right\}^{2}. \triangle K$$

In order to compensate for possible changes in the circuits with time, the distributed capacity of the other generator circuit is varied from outside by means of a rod with a small brass disk attached to it on the inside of the shield and fitted through an ebonite rod. Small changes in frequency can be obtained by turning this brass rod and thus varying the distance of the small disc from the generator circuit.

The Gas Condenser.

As brass and copper are found to be acted on by the organic compounds used in the investigation, pure nickel was chosen as the material of the condenser. For the sake of lightness and ease in manipulation the type of parallel plate system was finally adopted upon. Figure 2 shows the disposition of the condenser system.
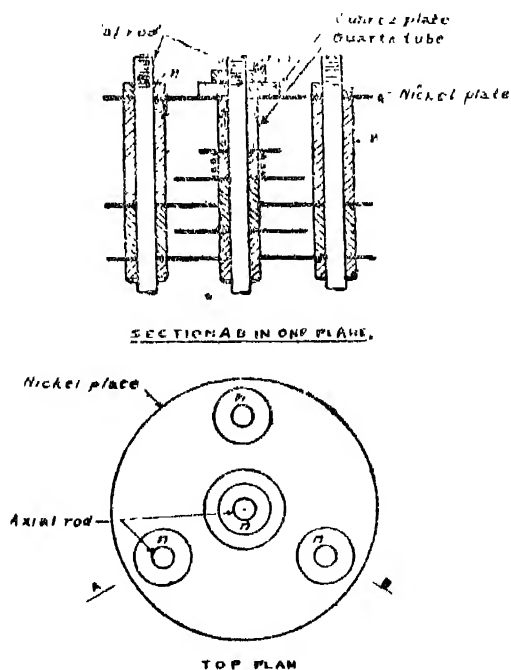
Fig. 2

The outer plate system.—It consists of 18 circular discs of 39 mm. in diameter and 0·5 mm. in thickness and has three

holes of 3 mm. diameter punched near about the circum-ference 120° apart from each other and three rods of pure nickel pass through the holes. Ring washers of the same material keep all the plates excepting the two outermost ones exactly 2·5 mm. apart. The frame is kept rigidly fixed with suitable nuts screwed on these rods. There is also another hole of 5 mm. diameter punched at the centre of the plates to allow the setting of the inner system.

The inner plate system.—It is composed of **17** circular discs of **17** mm. in diameter. All the discs are arranged parallel to each other and kept at a distance of 2·5 mm. with suitable washers.

Insulation.—At each end of the rod which forms the axis of the inner system a fused quartz tube is inserted for insulating the axis rod from the outermost plates of the other system and a fused quartz plate with a hole in its centre also slips upon the rod and keeps the plate *in situ.* A nut now fixes both the systems perfectly rigid with reference to each other. A spring washer is inserted in between the quartz tube and the first plate of the inner system, serving to release any strain that might be set up during the heating process.

The condenser is sealed in a glass tube fitted with a stop-cock and a capillary tube leads to the pump and gas system. The two platinum leads are sealed at the top.

Calibration.

It has been pointed out by Zahn and Watson[12] that the accurate determination of dielectric constants is largely a problem in calibration.

The calibration of the condensers were made in terms of the precision condenser by the method of substitution. As the value of the precision condenser is only 1134 $\mu\mu$F and the

12   H. E. Watson, Proc. Roy. Soc., 117 (1927).

fixed condenser of the order of $5000\mu\mu$F, the procedure of calibration was as follows. One $1000\mu\mu$F condenser was first calibrated in terms of the standard condenser. Two $2000\mu\mu$F condensers were next calibrated in terms of the standard condenser and the $1000\mu\mu$F condenser. Finally the $5000\mu\mu$F condenser was calibrated in terms of the standard condenser and the two $2000\mu\mu$F condensers.

To calibrate the $1000\mu\mu$F condenser, the standard condenser and the $1000\mu\mu$F condenser were placed in parallel by mercury cups, a fixed condenser of $500\mu\mu$F being inserted in series in place of the gas condenser. The two circuits were made to oscillate, the setting of the standard condenser being at a definite point. The frequency of the beats was adjusted to that of the tuning fork by varying the capacity of the other circuit. The $1000\mu\mu$F condenser was then removed and by varying the capacity of the precision condenser the former condition of no beat was restored. The change of readings of the precision condenser gave directly the value of the $1000\mu\mu$F condenser. This adjustment took nearly 3 to 4 minutes and conditions of the circuits remained unchanged during this period. The same procedure was adopted for the calibration of the $2000\mu\mu$F and $5000\mu\mu$F condensers.

Effective Value of the Gas Condenser.

The gross value of C was determined by inserting the condenser in parallel with K by means of mercury cups. The circuits were first adjusted to zero-beats, then C was inserted in parallel with K and the latter adjusted till the condition of zero-beats was restored. The difference of the readings on the precision condenser gave directly the value of C. This was found to be $125{\cdot}88\mu\mu$F.

The capacity due to the leads was determined by constructing two dummy leads of the same length and disposing them in the same manner as the actual leads. This was

found to be $5\cdot85\mu\mu$F. The capacity due to the portion of the dielectric space occupied by the quartz tube was also calculated to be $0\cdot15\mu\mu$F. Hence the total capacity which is not altered by the influx of the gas is $6\mu\mu$F. To obtain the alterable capacity, this must be subtracted from the total capacity $C = 125\cdot88\mu\mu$F. The final value for the alterable capacity, i.e., the effective value of the gas condenser is $C_o = 125\cdot88 -6 = 119\cdot88\mu\mu$F.

The final equation for the dielectric constant is

$$\epsilon - 1 = \frac{\triangle C}{C_o} = \frac{C^2}{C} \frac{\triangle K}{\{K + \tfrac{1}{2}\triangle K + K'\}^2}$$

$$= 132\cdot6 \frac{\triangle K}{\{K + \tfrac{1}{2}\triangle K + K'\}^2}$$

Temperature.

To avoid the presence of stray conductors anywhere near the gas condenser, Zahn's method of measuring temperature by means of platinum wire wrapped round the condenser was not followed. A copper—constantan thermo-couple was used. A galvanometer of voltage sensitivity of the order of $1\cdot7 \times 10^{-6}$ —was used for the detection of balance point against a Weston Standard Cadmium cell. The fall of potential per cm. of the potentiometer wire was adjusted so that a change of $0\cdot1°$C could easily be detected. The thermocouple was first standardised and the values obtained agreed very closely to that given by L. H. Adams.[13] For our measurement of temperature we would only measure the thermo e.m.f. in microvolts and, from Adam's table, determine the corresponding temperature. Steadiness of temperature was of more importance than its absolute value. An oil-bath of large capacity and heated electrically was used and the temperature control of the apparatus was found very satisfactory. In order to be

    [13] L. H. Adams, Am. Inst. Min. and Met. Eng. (Pyrometry), (1920) 165.

sure of the steadiness of temperature attained by the conden-ser the bath was heated at a particular current for at least twenty hours.

Pressure.

The pressure of the gas in the experimental condenser was read from the height of the mercury manometer with the help of a Kathetometer from a distance to an accuracy of 0·5 mm.

Method of Measurement.

The steadiness of temperature of the bath was first tested at the interval of half-an-hour. When the bath had attained the steady temperature, the oscillators were started and allow-ed to work for at least half-an-hour previous to taking any measurement. When conditions were steady, the condenser was evacuated and the setting of K for zero-beats was then noted. The vapour was next introduced into the condenser C, K adjusted to zero-beats again, and the new setting of K noted. The pressure of the vapour inside the experimental condenser was determined by noting the mercury levels in the manometer just before and after the introduction of the vapour. The whole observation takes nearly three minutes, during which the conditions of the circuit remained steady. At each temperature, generally 5 to 10 observations were made.

Measurements were first made on dry CO_2-free air as a check on the behaviour of the apparatus and the correctness of calibration. This measurement was repeated before and after taking the observations on each vapour. The dielectric constant of air was found to agree well with the values of Zahn and Sanger.

The readings were usually taken during night when there was no external source of disturbance in the building and the slightest change from the condition of zero-beats could easily be detected.

6

Results.

The chemicals were brought from Kahlbaum.   (Purest.)

TABLE I

Vapour	$(\epsilon-1)\ 760$	$\dfrac{(\epsilon-1)\ P_0 T^2}{P}$	T^o
CH_3I	·009358	865	304°
(B. P. 43°C)	·008376	901	328
	·007527	943	351
	·006153	1007	395
C_2H_5Br	·009640	885	303°
(B. P. 38°C)	·008728	893	320
	·007482	910	356
	·006120	929	390
C_2H_5I	·012360	1262	319·5
(B. P. 72°C)	·011980	1282	327·5
	·011120	1316	344·0
	·010410	1340	358·5
	·008911	1415	397·5

TABLE II

Vapour	$(\epsilon-1)_0$	$\mu \times 10^{18}$
CH_3Cl*	...	1·69
CH_3I	·005761	1·313
C_2H_5Cl*	...	1·98
C_2H_5Br	·002200	1·779
C_2H_5I	·007839	1·620

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* See S. C. Sircar, Indian Jour. Physics, Vol. 3, following paper.

A graph showing the relation between $(\epsilon - 1)\dfrac{P_0 T^2}{P}$ and temperature is given in Fig. 3.
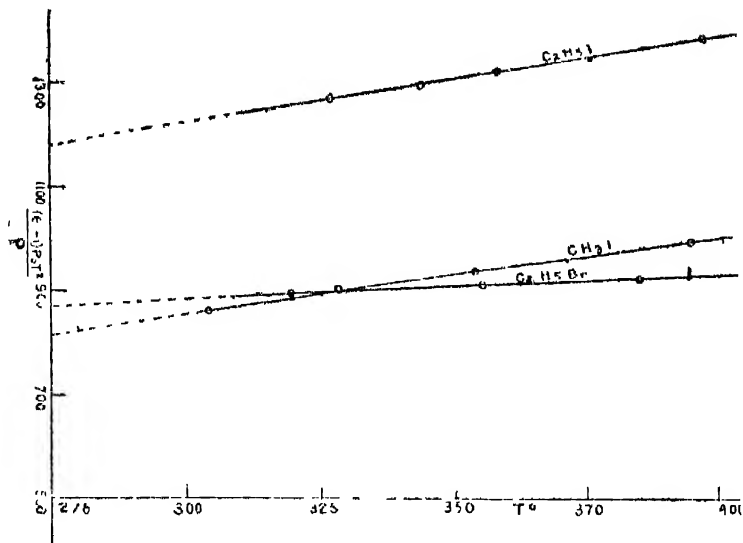
Fig. 3

Discussion.

While discussing the dielectric constants of the group CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, Sänger has pointed out that the configuration of CH_4 can be taken as a regular tetra-hedon with the C-atom at the centre of gravity and H-atoms lying at the four corners of it. The validity of such assumption has also been substantiated by Dennison,[14] who determined the normal modes of vibration of the nuclei of CH_4, and found that there is a close co-relation of these normal frequencies with the fundamental frequencies of the rotation oscillation bands of methane determined by Cooley.[15]

Considering now the cases of HCl, HBr, HI, whose electric moments have been determined by Zahn it is noticed that the assymmetry of the halogen halides is gradually lessened as

[14]   Dennison, Astro. Journal, 62, 84 (1925).

[15]   Cooley, Astro. Journal, 62, 73 (1925).

halogens of higher atomic weights are substituted in the molecule.

$$HCl - 1 \overset{\mu}{\cdot} 034 \times 10^{-18}$$
$$HBr - 0 \cdot 788 \times 10^{-18}$$
$$HI - 0 \cdot 382 \times 10^{-18}$$

The effect on the magnitude of the permanent dipole by the substitution of an atom of the same group in the periodic table but of higher atomic weight is also noticed in the case of NH_3, PH_3 and AsH_3 whose moments have recently been investigated by H. E. Watson. Thus

$$NH_3 - 1 \overset{\mu}{\cdot} 51 \times 10^{-18}$$
$$PH_3 - 0 \cdot 54 \times 10^{-18}$$
$$AsH_3 - 0 \cdot 18 \times 10^{-18}$$

In the case of organic vapours examined by us we also notice that the strongest assymmetry is found in the case of chlorides and weakest in the iodides, the bromides occupying an intermediate position in the case of both methyl and ethyl groups.

Kemble [16] has recently discussed the nature of the typical polar molecules having permanent dipole moments. It is assumed that the molecules of this type are held together by electrostatic forces. There is evidently the attraction of the outer electron system of the components of the molecules on the nuclei and also the repulsive force of the nuclei among themselves varying inversely as some power of the inter-molecular distance. There is sufficient reason to consider at least in the case of hydrogen halides that the hydrogen nucleus penetrates the outer boundary of the valency electrons of the negative ion. The H^+-ion enters a region where the force of repulsion of the halogen nucleus is kept in balance by the attractive force of the outer electrons. The mean radius of the

[16]   Kemble, Bull. National Research Council, 57 (Mol. Spectra in Gases).

sphere of the outermost group of electrons of the chlorine ion is taken to be 0.95×10^{-8} cm. when it is undistorted by the presence of H^+-ion and since the internuclear distance of HCl has been determined by Imes to be 1.279×10^{-8} cm. it is reasonable to assume as a first approximation that the H^+-ion has penetrated into the chlorine ion. The electric moment of the dipole which is due to a proton and an electron nearly 10^{18} cm. apart, indicate that this must come from the loosely attached electrons of the negative ion which have been distorted due to the action of the H^+-ion.

In the case of HBr molecule the nuclear distance has been increased to 1.418 but the distortion of the outer shell of electron has not been so much as in the case of HCl and its moment is reduced to 0.788×10^{-8}. In the case of HI, the distortion is still less and the moment has been reduced to 0.382×10^{-18}.

But since the internuclear distance gradually increases, as we pass from Cl to Br and then to I, the total polarisability has increased.

The case of organic halides which we considered is however a little more complicated. For want of sufficient data we cannot reasonably assume that the $CH_3{}'$ or $C_2H_5{}^+$-ion has gone inside any of the electronic shells of the Cl, Br or I.

Debye[17] has suggested another model which can explain the formation of such stable molecules. He considers that the negative charge due to free electron of the halogen ions when brought in close proximity to the halogen atom will tend to execute forced oscillations with the period of the orbital motion of its valency election and the phase of this vibration will be such that the distance between the free electron and orbital electron is least when the latter is at the nearest point of the path. The orbital electron will tend to slow down and the time average of the repulsive force will be increased.

[17]   Debye, Phys. Zeit., 22, 302, 1921.

Thus we can expect that a positive ion of the type of CH_3^+ or $C_2H_5^+$ when confronted with a negative ion of halogens such as Cl^-, Br^-, or I^-, will be under the mutual electrostatic action of opposite charges and they will form a stable polar molecule with the oscillating of electron encircling both the systems.

But we should consider the change in shapes of the electron orbits. The measure of the actual extent of the distortion of the orbits is still not available but one can reasonably suppose that the distortion of the halogen outer shells will be less as we proceed from chlorine of lowest atomic weight to iodine of the highest. The contribution of the moment due to carbon atom as under the influence of the other hydrogen atoms will remain sensibly the same. As a resultant we would expect gradually diminishing dipole moment of the molecules with the increase in the atomic weight of the halogen ions. The polarisability of the molecule will evidently increase with the increase in atomic weight of the halogen ion as has also been noticed in the hydrogen halides.

Experiments are in progress to determine the increase in distance of the group $C-Cl$, $C-Br$ and $C-I$ with the help of the analysis of the fine structure of the rotation vibration spectrum of these molecules.

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The Electric Moments of CH_3Cl, C_2H_5Cl and $CHCl_3$.

BY

S. C. SIRCAR, M.Sc.

ABSTRACT.

The paper describes measurements of the dielectric constants of CH_3Cl, C_2H_5Cl and $CHCl_3$ vapours at different temperatures by heterodyne null method. The results entirely support Debye's dipole theory, the values of the permanent moments calculated on the basis of this theory being for CH_3Cl $1·69 \times 10^{-18}$ for C_2H_5Cl $1·98 \times 10^{-18}$ and for $CHCl_3$ $1·05 \times 10^{-18}$ (all in e. s. u.). The values are compared with those obtained from optical data, and by the same method by other workers, and discussed.

Introduction.

The dielectric constant of a few vapours and gases at different temperatures has been measured by Zahn,[1] Sänger,[2] Watson[3] and others by heterodyne null method and it has been observed that for these vapours and gases Debye's equation

$$\frac{\epsilon-1}{\rho} \times T = aT + b$$

is satisfied. From this equation the permanent electric moments of the molecules have been obtained, the magnitude of which is the same as indicated by Debye's theory, *i.e.*, of the order of product of charge on an electron and the linear

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[1] O. T. Zahn, Phys. Rev., 24, p. 400, 1924; 27, p. 455 (1926).

[2] R. Sänger, Phys. Zeit., 27, p. 556, 1926; 28, p. 455 (1927).

[3] H. E. Watson, Proc. Roy, Soc., 117, p. 43 (1927).

dimension of a molecule. This method, therefore, can give a fairly accurate value of the permanent moment. It has been shown recently by Raman and Krishnan,[1] that the permanent moment μ can also be obtained by an entirely different method. It is well-known that for a vapour obeying Boyle's Law, the Kerr constant

$$K = \frac{n_p - n_s}{\lambda E^2} = \frac{3\pi\nu}{\lambda} \cdot (\theta_1 + \theta_2) \qquad \ldots \quad (1)$$

where $\nu =$ no. of molecules per unit volume
$\lambda =$ wave length of incident light
$E =$ acting electric field

n_p and n_s are the refractive indices for light vibrations along and perpendicular to the field.

$$\theta_1 = \frac{1}{45kT} [(A-B)(A'-B') + (B-C)(B'-C') + (C-A)(C'-A')] \quad (2)$$

and $$\theta_2 \equiv \frac{1}{45k^2T^2} [(A-B)(\mu_1^2 - \mu_2^2) + (B-C)(\mu_2^2 - \mu_3^2) +$$
$$(C-A)(\mu_3^2 - \mu_1^2)] \qquad \ldots \quad (3)$$

where k is the Boltzmann constant per molecule, T is the absolute temperature, A, B, C are moments induced in the molecule along its three principal axes of optical anisotropy by unit electric field in the incident light waves acting respectively along these directions, A', B', C' are similar moments induced in the same three directions by unit electro static field and μ_1, μ_2, μ_3 are the components along these directions of the permanent electric moment of the molecule. The six constants A, B, C and A', B', C' can be reduced to three by assuming that $\dfrac{A'}{A} = \dfrac{B'}{B} = \dfrac{C'}{C} = \dfrac{\epsilon - 1}{n_0^2 - 1}$ where for polar molecules

[1] C. V. Raman and K. S Krishnan, Phil. Mag., Vol. III, 714 (1927).

ϵ is the contribution to the dielectric constant from the induced electric moment alone, θ_1 is thus proportional to $(A-B)^2+(B-C)^2+(C-A)^2$ and this can be evaluated in terms of r, the factor of depolarisation of the transversely scattered light, by optically anisotropic molecules from the relation

$$r=\frac{6\left[(A-B)^2+(B-C)^2+(C-A)^2\right]}{10\left[\frac{3(n_0-1)}{2\pi\nu}\right]^2+7\left[A-B)^2+(B-C)^2+(C-A)^2\right]}$$

so that

$$\frac{3\pi\nu}{\lambda}\theta_1=\frac{3(n_0-1)(\epsilon-1)r}{4\pi\nu\lambda kT(6-7r)} \qquad \ldots (4)$$

In the simple case when the optical ellipsoid is a spheroid of revolution, $B=C$ and

$$\theta_2=\pm\frac{(n_0-1)\mu^2}{30\pi\nu k^2 T^2}(2\cos^2 a-\sin^2 a)\sqrt{\frac{5r}{6-7r}} \qquad \ldots (5)$$

where a is the angle between the A axis and the permanent moment. From (1), (4) and (5) μ can be calculated when the optical constants and the angle a are known or if μ be determined accurately by any other method the value of a can be found out. It has been shown by Raman and Krishnan[1] in the said paper that the value of μ for HCl molecule calculated by this method agrees remarkably with that obtained by Zahn[2] by the method of dependence of dielectric constant on temperature. But the value of μ for CH_3Cl determined recently by Sänger[3] by the same method is about 17% higher than that obtained from optical constants with the assumption that $a=0$. In the present paper, an account of the determination μ for CH_3Cl, C_2H_5Cl and $CHCl_3$ is given.

[1] C. V. Raman and K. S. Krishnan, *loc. cit.*

[2] C. T. Zahn, *loc. cit.*

[3] R. Sänger, *loc. cit.*

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Technique.

The technique used is similar to that used by Zahn. The oscillating circuits were maintained by Mullard's P. M. 4 valves with anode voltage of 70 volts and a grid bias of 4 volts in each of the circuits. The oscillating loops were placed in the anode circuit, the inductance in the same consisting of about 10 turns of S. W. G. No. 20 D. S. C. wire wound on a glass tube of diameter about 4 cms. The inductance in the grid circuit consisted about 200 turns of S. W. G. No. 26 D. S. C. wire wound on a glass tube of diameter about 2·5 cms. All the circuits including the receiving set were completely shielded with earthed zinc sheets and negative sides of the filaments of all the valves were connected to the shielding box. The gas condenser and the headphone were outside the shielding box and leads passed through holes in zinc sheets. The grid of the detecting tube remained floating in the chambers containing the oscillating circuits. The capacity of the variable air condenser of capacity about ·0005 μF of the circuit used as the fixed oscillating circuit and that of the measuring condenser of the other oscillating circuit could be adjusted from outside by means of long shafts attached to the axle of the moving vanes. Very small change in capacity of the fixed circuit could be effected by the movement of a brass cross piece attached to a long shaft which could be turned from outside. The gas condenser was a cylindrical copper condenser. The inner cylinder was made by turning on lathe a solid copper rod so that the narrow portions at the ends were of diameter about 5 mm. and provided with screw threads. The outer cylinder was made by turning a seamless copper tube so that finally its length was about 16 cm., its diameter was about 3 cm., and its thickness was about 1 mm. The difference between the diameter of the inner cylinder and that of the inner surface of the outer cylinder was about 1·5 mm. The outer cylinder was provided with tight fitting

caps each provided with a hole at the centre of diameter about 7 mm. The two cylinders were mounted coaxially and held in position, insulated from each other by means of two nuts pressing against two mica discs of diameter about 1 cm. These mica discs fitted in grooves in the caps surrounding their central hole and were provided with central holes of diameter about 5 mm. in which fitted the narrow ends of the inner cylinder. The two cylinders were provided with two copper terminals to which tungsten leads were soldered. Gas could be introduced into the interspace through a small hole in one of the caps. A platinum wire of resistance about 24 ohms was wound on the condenser, mica sheets being used for insulating the wire from the condenser. The ends of the platinum wire were soldered to tungsten leads. The condenser was then sealed in a pyrex tube, the four leads being taken out through one end of the tube which was provided with a narrow side tube connected to a mercury manometer, the vessel containing the experimental liquid or the vapour and to a cenco Hyvac pump. The gas condenser was placed outside the zinc box in an earthed copper cylinder which was covered with asbestos sheet on which the heating coil was wound. The platinum thermometer was standardised by measuring its resistance in melting ice, in steam and in boiling sulphur. A bridge wire of resistance one ohm connected in series with a P.O. Box corresponded to a range of about 18°C so that the temperature could be measured correct to at least $0\cdot5^\circ$C allowing for error in calibration. The measuring condenser was an 1186 Bureau of Standard type standard air condenser of maximum capacity 1134 $\mu\mu$F manufactured by Leeds and Northrup Company. According to the certificate of the manufacturers, the readings are correct to $\pm$ 1 $\mu\mu$F, so that for small capacities, an accuracy of about $0\cdot5\%$ in the reading can be expected. The whole scale is divided in 100 divisions and $\frac{1}{10}$th of one such division can be read with the help of a vernier

and this corresponds to about 1·08 $\mu\mu$F. The capacities of the gas condenser and of the mica condenser K' placed in series with the gas condenser and parallel to the measuring condenser were such that a change of about 1000 $\mu\mu$F in the capacity of the measuring condenser was required to annul the effect of a change of 1 $\mu\mu$F in the gas condenser so that a change of $\frac{1}{1000}$ $\mu\mu$F in the capacity of the gas condenser could be measured. The mica condenser connected parallel to the measuring condenser consisted initially of a set of dubilier condensers but finally a Macmichæl condenser marked ·01μF was used. A valve maintained tuning fork of frequency about 800 was used as the source of standard note to which the beat note was tuned. The frequency of the oscillating circuits as determined by a wavemeter was about 1·3 × 10^6.

Experimental.

The gas condenser was calibrated by connecting it in series with the variable standard condenser in one of the oscillating circuits as shown in Fig. 1 and short circuiting first the standard condenser and then the gas condenser.
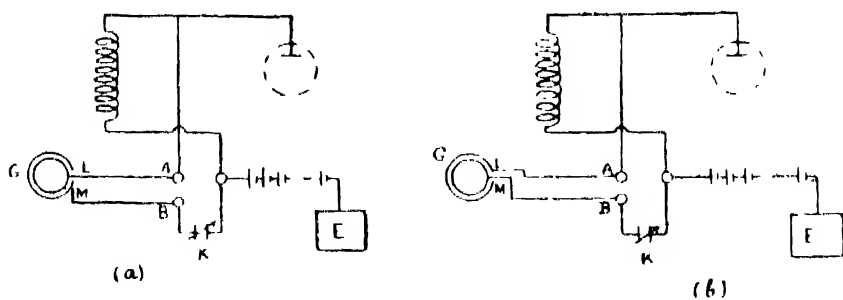
Fig. 1

The length of each of the leads AL and BM were about 50 cm. It was found that its capacity was different for the two connections indicated in Fig. 1(a) and (b). When the inner

cylinder was connected to the anode direct, the capacity deter-
mined by short circuiting the gas condenser at the points AB
was $299\cdot0\mu\mu F$ and for connections shown in Fig. 1 (b) it was
$320\cdot0\mu\mu F$. This capacity when determined by short circuit-
ing the gas condenser at the points L and M, just near the
ends of the tungsten leads was $294\cdot1$ for connections shown
in Fig. 1 (a) and $315\cdot0\ \mu\mu F$ for the other arrangement. Thus
the value obtained for the case shown in Fig. 1 (a) was always
higher. There was also another difficulty in case of the
arrangement shown in Fig. 1 (b). It was observed that in
this case movement of any conductor or variation of current
in any other circuit connected to the mains in the room
changed the pitch of the beat note whereas no such difficulty
was observed in the other arrangement. The connections
shown in Fig. 1 (a) were therefore preferred to avoid stray
capacities and the capacity of the gas condenser between the
points L and M was found to be $294\cdot1\ \mu\mu F$ and this was
assumed to be the capacity C_0 altered by the introduction of
the gas, the capacity due to the mica discs and that between
the tungsten leads being neglected. The distance between
the inner surface of the cap and the end surface of the inner
cylinder was about 8 mm., so that the capacity due to the thin
annular mica disc was negligible. The capacity C of the gas
condenser between the points A and B including that due to
leads was found to be $299\cdot0\ \mu\mu F$, so that the quantity

$$\frac{C^2}{C_0}=304\ \mu\mu F.$$ The gas condenser being connected as in Fig.

1 (a) each of a set of dubilier mica condensers marked $\cdot001\mu F$,
$\cdot001\mu F$, $\cdot003\mu F$ and $\cdot006\mu F$ was calibrated by placing it in
place of the standard measuring condenser and then substitu-
ting it by the standard condenser either alone or connected in
parallel with the smaller capacities of the set already calibra-
ted. The capacity of Macmichæl mica condenser marked
$\cdot01\ \mu F$ was then determined with the help of this set by

substitution method as before. The capacity was found to be
·0101μF. The same as determined with the help of a Farad
bridge manufactured by Leeds and Northrup Company was
found to be ·0102 μF. The value ·0101 μF was taken in cal-
culations. The dielectric constant of dry CO_2 free air was then
determined with this arrangement and the value of $\epsilon - 1$
obtained when reduced to 760 mm. of pressure and 0°C was
·000552.

The gas condenser was heated and kept at temperature of
about 250°C for about six hours and the occluded gas was
continuously pumped out. While the temperature of conden-
ser was changing there was a slow drift of frequency and
readings could be taken only when the temperature was con-
stant. The vapour was introduced at least an hour after the
temperature was steady. The platinum thermometer was
disconnected from the P.O. Box when readings were taken.
In case of C_2H_5Cl and $CHCl_3$ the liquids obtained from
Merck and Kahlbaum respectively were placed in glass bulbs
provided with taps by opening which the vapour could be
introduced into the pyrex tube containing the gas condenser.
The residual air in the bulb was first driven out before the
vapour was introduced in the condenser. Methylchloride
vapour was obtained by breaking a Merck's capsule containing
the liquid, in a sealed copper vessel provided with a stopcock.
The vessel was evacuated for about 12 hours in order to get
rid of the occluded gases before the capsule was broken. For
taking reading at any temperature the pyrex tube containing
the condenser was evacuated, beat note in the headphone was
tuned to the note of the tuning fork, the vapour was intro-
duced by opening the tap of the bulb for a short time and
closing it again and the beat note was again tuned to the tun-
ing fork by adjusting the measuring condenser. The
pressure of the vapour was measured with the help of a
cathetometer. In case of chloroform the tap of the bulb had
to be kept open in order to keep the pressure constant while

the reading was being taken. The time required for taking a reading did not exceed one minute and the drift of frequency of the beat note during this time was quite negligible. $\epsilon-1$ at the pressure of the experiment was calculated from the relation

$$\epsilon-1=\frac{C^2}{C_o} \cdot \frac{\triangle K}{(K'+K+\frac{1}{2}\triangle K)^2}$$

where K′ is the capacity of the mica condenser and $\triangle K$ is the change in the capacity K of the measuring condenser required for annulling the effect of change in the capacity of the gas condenser on the total capacity in the oscillating circuit. The density ρ at temperature T and pressure P was converted to ρ_o at 760° and 0°C by assuming that the gas law $\frac{P}{\rho T}=$ Const. was obeyed. The quantity

$$(\epsilon-1) \times \frac{760}{P} \times \frac{\mathsf{T}}{273} \times \mathsf{T}$$

was plotted as shown in Fig. 2 against T where T and P denote the temperature and pressure for each reading. The permanent moment μ was obtained from the relation

$$(\epsilon-1)\frac{760}{\lambda} \cdot \frac{\mathsf{T}}{273} \times \mathsf{T}=a\mathsf{T}+b$$

where

$$a=\frac{\rho_o}{M} \cdot 4\pi N\gamma, \qquad b=\frac{\rho_o}{M} \cdot \frac{4\pi N\mu^2}{3k}$$

M = Molecular weight of the substance
N = 6 06 × 10²³
k = 1·37 × 10⁻¹⁶

The intercept on the Y axis in Fig. 2 was measured and μ was calculated from the relation

$$\mu^2=b \times \frac{M}{\rho_o} \times \frac{3k}{4\pi N}=b \times 1\cdot209 \times 10^{-30}$$

Table I shows the results in a tabulated form and in Table II and Fig. 3 is shown the variation of $\epsilon-1$ with pressure at constant temperature.

Results.

TABLE I.

Vapour.	Temperature T	Pressure in mm. of Hg. P.	$\epsilon-1$ at frequency $1\cdot3\times10^6$	$(\epsilon-1)\dfrac{760}{P}$	$(\epsilon-1)\dfrac{760}{P}\dfrac{T^2}{273}$	$\mu\times10^{18}$
CH_3Cl	291·5	68·8	·000862	·00953	2·96	
	357·2	186·0	·001583	·00645	3·01	1·69
	411·3	104·8	·000703	·00510	3 16	
	474·2	95·5	·000503	·00400	3·29	
C_2H_5Cl	296·5	82 0	·001365	·01268	4·08	
	357 2	152·4	·001835	·00915	4·27	1·98
	415·0	195·5	·001801	·00701	4·42	
	474·2	183·5	·001346	·005573	4·59	
$CHCl_3$	297·0	150·0	·001097	·00556	1·797	
	387·9	148·0	·000721	·003705	2 04	1·05
	410 9	162 8	·000733	·00312	2·114	
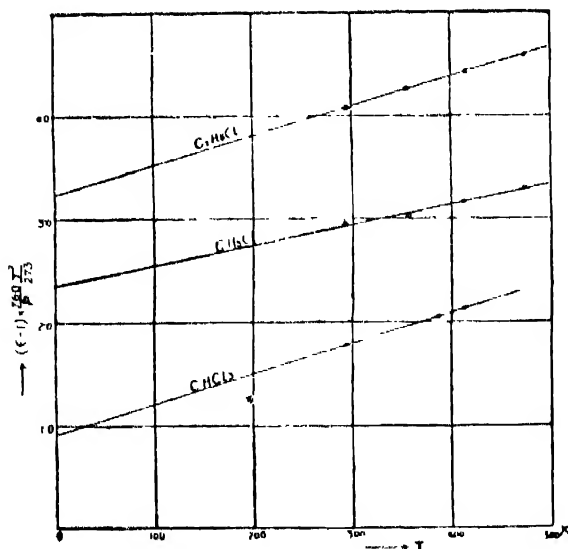
Fig 2.

TABLE II.

CH$_3$Cl (T=357·2)		C$_2$H$_5$Cl (T=357·2)	
Pressure in mm. of Hg.	$\epsilon-1$	Pressure in mm. of Hg.	$\epsilon-1$
90·5	·000758	82·3	·000981
102·0	·000853	120·9	·00147
120·0	·001007	152·4	·001835
139·0	·001186	162·7	·00196
186·0	·001583	206·6	·002496
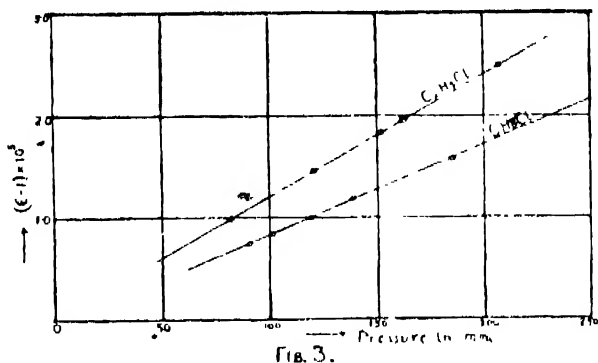
Fig. 3.

Discussion.

The value of μ for CH$_3$Cl is $1·69 \times 10^{-18}$ and agrees fairly well with the value $1·66 \times 10^{-18}$ obtained from optical data. For C$_2$H$_5$Cl the value of μ obtained is $1·98 \times 10^{-18}$ whereas the same calculated from optical data is $1·76 \times 10^{-18}$ and the difference is probably beyond the limits of experimental error. The assumption made in calculating μ from optical data, that the angle α between A axis of the optical anisotropy and the permanent moment is zero, does not seem to be rigorous. The value of α with μ as $1·98 \times 10^{-18}$ is about $22°—6'$. In case of chloroform readings were taken only at three temperatures and μ obtained from these three points is $1·05 \times 10^{-18}$ and the same obtained by Sänger is $0·95 \times 10^{-18}$. It is quite evident

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from the observation of various authors that there are many sources of error in this method for the determination of dielectric constant and the absolute value of the same as obtained by different observers may vary widely and consequently the value of permanent moment obtained by this method is not very accurate. The value of μ obtained from optical data for simple molecules however is more reliable because μ being proportional to $\dfrac{K^{\frac{1}{2}}(6-7r)^{\frac{1}{4}}}{(n_0-1)^{\frac{1}{2}}(5r)^{\frac{1}{4}}}$ any error in the determination of any of these optical constants would not affect μ very much. All the values obtained by the author would be too low if there had been any error in calibrating the gas condenser. But as the value of dielectric constant of air obtained with this arrangement agrees fairly well with the values of other observers and as the value of permanent moment obtained for $CHCl_3$ is slightly higher, instead of being lower, than that obtained by Sänger,[1] it is quite evident that the gas condenser has been calibrated fairly accurately. Any trace of impurity in Merck's CH_3Cl would not affect μ very much, because an error of even 10% in the absolute value of dielectric constant does not change the value of μ by more than 5%. The difference between the values of μ for CH_3Cl obtained by Sänger and author is about 16% and it seems that the value obtained by Sänger is a little too high.

In conclusion, the author wishes to express his thanks to Prof. C. V. Raman for kindly suggesting the problem and taking keen interest during the progress of the work. The author's thanks are also due to Mr. K. S. Krishnan for his helpful suggestions and to Prof. P. N. Ghosh for kindly lending him the standard air condenser.

[1] R. Sänger, *loc. cit.*

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The Diffraction of X-rays by Aqueous Solutions of Canesugar, Levulose and Glucose.

BY

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ABSTRACT.

X-ray diffraction of canesugar, levulose and glucose both in the powder form and in their aqueous solutions at different concentrations has been studied, using the Cu Kα radiation. A dilute solution of a sugar gives a pattern consisting of the outer ring due to the water, and a corona which immediately surrounds the central spot, and is due to a relatively intense scattering at small angles. With increasing concentration of the solution, the corona increases in intensity till a concentration of about one part of sugar to one of water is reached. This corona is attributable to the molecules of the dissolved substance which are distributed at random in the solvent much in the same way as gaseous molecules. These dissolved molecules give rise to a scattering which is large at small angles and decreases at larger angles. The gaseous state of the dissolved substance in a dilute solution which was deduced long ago by Van't Hoff from considerations of osmotic pressure, thus finds a direct experimental verification by means of X-ray diffraction. At a concentration higher than 1 : 1, however, the corona is modified and develops into a halo on account of a marked diminution of the intensity of scattering at small angles. This phenomenon may be interpreted as due to the dissolved molecules in a concentrated solution acquiring an approximately uniform spatial arrangement, and in consequence, the scattered waves at small angles destroying each other's effects by interference. At still higher concentrations, the

halo develops into a well-defined ring with a clear space at the centre, the ring increasing in diameter with increasing concentration. The pattern for the most concentrated solution examined is very much like the pattern for the powder.

The angular radius of the disk surrounding the central spot just before it develops into a ring, gives us a measure of the average size of the dissolved molecule which agrees fairly well with the calculated value. Thus, in solutions containing the same quantities of the solutes, the disks round the central spot produced by levulose and glucose molecules are spread out over a greater area than that for canesugar. An attempt is made to connect these facts with the thermodynamic theory of the fluctuations of density and concentration in solutions. The influence of the hydration of the molecules in solution is also considered.

Theoretical.

While a vast amount of experimental work has been done to elucidate the nature of crystalline solids and of pure liquids by means of X-rays, our knowledge of the nature of solutions as revealed by this method is very meagre. Wyckoff[1] examined saturated solutions of iron ammonium alum and of potassium chloride using the K_a-rays from molybdenum, but found that the patterns for the aqueous solutions were identical with that given by water alone. In a previous communication, the present writer examined aqueous solutions of acetamide and of ammonium nitrate of different concentrations, using the copper K_a-radiation, and compared their X-ray patterns with those obtained in the solid state, and in the case of acetamide, in the molten state also.[2] It was shown that the patterns for the aqueous solutions were quite different from that for pure water. For instance, in very concentrated solutions, ammonium nitrate formed a ring of its own which was just smaller than the water ring. As the dilution increased, this ring became smaller, fainter and more diffuse,

[1] Wyckoff, Amer. Jour. Sci., 5, 455 (1923).
[2] Krishnamurti, Ind. Jour. Phys., 2, iv, 501 (1928).

and at a dilution of 1 : 4 existed only as a general scattering inside the water halo. In the case of acetamide, the inner ring was fainter, and disappeared more quickly with dilution, while the outer ring joined up with the water ring. The general scattering inside the halo in dilute solutions of these substances was interpreted as due to the random distribution of the solute molecules just as in the gaseous state, its faintness and its distribution over a large area being occasioned by the small size of the molecules distributed at random in the solution.

The present investigation was undertaken to verify the general conclusions stated above, using bigger solute molecules for this purpose. Moreover, the solute should be a non-electrolyte, nonvolatile and easily soluble in water. A very suitable substance for this work was found in canesugar, one of the first substances to be used in demonstrating the osmotic pressure of solutions. Canesugar was therefore examined both in the solid state as a crystal powder as well as in solution at various concentrations up to about three parts of sugar to one of water. A remarkable series of photographs was obtained which portrayed all the changes which take place from the solid state to the state of a very dilute solution, in a very vivid manner.

It is well-known that in a very dilute solution containing a nonvolatile solute like canesugar, the molecules are distributed at random just as in the gaseous state. Van't Hoff made use of the experimental data of Pfeffer on the osmotic pressure of solutions, and showed that there exists an analogy between the osmotic pressure of a dilute solution and the gaseous pressure that the solute would exert if it existed in the form of a gas in the volume occupied by the solution. The experimental results of Pfeffer showed that the osmotic pressure is directly proportional to the concentration, a relation which corresponds to Boyle's law for gases. Moreover this law holds good only for dilute solutions and notable deviations

have been noticed in concentrated solutions, analogous to the deviations from Boyle's law for gases at high densities.

X-ray diffraction of the aqueous solutions of the sugars gives a convincing experimental verification of the validity of the above conclusions. In a very dilute solution of canesugar, we find that in addition to the water ring, there appears a general scattering, confined to a small region round the central spot, having the characteristic appearance of a corona. The intensity of this diffraction disk increases with an increase in concentration of the solution until it contains almost equal quantities of the solvent and solute. At higher concentrations, there is considerable diminution of scattering at small angles, and the disk develops into a well-defined ring.

These observations find some analogies in the case of light-scattering. It is a common observation that when the sun or moon is observed through a thin fog, it appears to be surrounded by a circular disk, due to diffraction by randomly distributed particles of water. Similarly, a diffraction disk surrounds a source of light seen through a plate of glass covered with a layer of dust. In a similar way, we can explain the corona observed round the central spot in the X-ray diffraction pattern of a dilute solution of sugar as due to scattering by the molecules of the solute which are distributed at random in the solution. That this is a true gaseous scattering is shown by considering its intensity at different concentrations, when it can be seen that for solutions up to a maximum concentration of about 1 : 1, the amount of scattering increases with concentration. This is again analogous to the scattering of light by gases, where the total amount of scattering is proportional to the number of molecules per unit volume in the case of an ideal gas (Raleigh Law of Scattering). Since the molecules are here distributed at random, the phases of the waves starting from the solute molecules are entirely uncorrelated, with the result that no interference is possible, and the total intensity is given by

adding the effects due to all the molecules. This scattering will extend in the case of X-rays to very small angles since the distance between the molecules is varying and can have any large value. A similar observation arises in the diffraction of light when it passes through a large number of small, equal but irregularly distributed apertures, or of a large number of equal circular discs in an opaque screen, when it may be shown that the total intensity is the same as that produced by a single aperture multiplied by the number of apertures. Similarly, the intensity of X-ray diffraction at small angles of scattering in the case of dilute aqueous solutions of sugar, where the solute molecules may be expected to be distributed at random, is simply the integrated energy of the scattered radiation in all directions multiplied by the number of molecules of sugar in unit volume. It can be seen very clearly from the photographs of the different solutions of canesugar, levulose and glucose, that the intensity of scattering at small angles falls off with the dilution, showing that it is a function of the number of molecules of sugar per unit volume, which, in addition justifies the assumption made, that the molecules are distributed at random. In the case of levulose and glucose, the same effects are observed as in canesugar, but due to the smaller size of the molecules, the intensity of scattering is less, and it is distributed over a larger area.

With an increase in concentration of more than 1 : 1 by weight, the corona develops into a ring, and there is very little scattering at small angles. In more concentrated solutions, the ring becomes more well-defined and increases in size, the scattering within the ring being very small. This is no doubt due to the fact that in very concentrated solutions the assumption that the molecules are distributed chaotically does not hold good, and they should be expected to possess an approximate spatial arrangement. This leads to destructive interference of the scattered waves, resulting in a diminished scattering near the central spot, and producing a definite ring.

An analogous case in light-scattering is that recently studied by Sogani,[3] that if the particles of an emulsion are of uniform size much larger than the wavelength of light ($d =$ 0· 002 cm.), and closely packed, a monochromatic beam of light passed through such an emulsion gives rise to diffraction rings surrounding the beam, with practically no scattering within the ring. The uniformity in the spatial distribution of the closely packed particles produces this destructive interference between the waves scattered by the particles. When the diffracting particles are separated by a sufficiently large distance, we can expect the appearance of a diffraction disk in this case also.

Raman and Ramanathan[4] have extended the statistical-thermodynamical theory of Einstein and Smoluchowski to the X-ray region, and have given a general explanation of the diffraction effects in pure liquids, by assuming thermal fluctuations of density just as in the analogous case of light-scattering. They have shown that at very small angles of scattering, the medium can be regarded as a ' structureless continuum,' and the same considerations as in the case of light apply here also. For larger angles of scattering, they deduced the formula :

$$I = C_1 \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \, \lambda_0^3 \, \left(1 - \frac{\lambda_1^3}{\lambda_0^3} \right)^2 \right\}$$

where β is the isothermal compressibility, λ_0 the mean molecular distance, C_1 a constant, and λ_1 obtained from the Bragg formula :

$$\lambda = 2\lambda_1 \, \mathrm{Sin} \, \frac{\theta}{2}$$

[3] Sogani, Phil. Mag., 1, 321 (1926).
[4] Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., 8, ii, 127 (1923).

The maximum intensity of scattering occurs when $\lambda_1 = \lambda_0$ and therefore lies in the direction θ_0 given by the formula :

$$\lambda = 2\lambda_0 \ \mathrm{Sin} \ \frac{\theta_0}{2}.$$

Hence the maximum corresponds to the wavelength λ_0 equal to the mean distance between neighbouring molecules. The values of λ_0 found experimentally agree very well with those calculated theoretically.[5]

In the case of solutions containing two components, there are not only fluctuations of density, but also considerable fluctuations of concentration. In an aqueous solution containing a nonvolatile solute, the fluctuations of density are smaller than the fluctuations of concentration, since the compressibility of the solution is very small. The fluctuations of concentration, in turn depend upon the rate of change of osmotic pressure $\frac{\partial P}{\partial K}$ with concentration. Where this factor begins to increase sensibly, we can expect smaller fluctuations of concentration. If we compare the values of $\frac{\partial P}{\partial K}$ for canesugar calculated from the values of Frazer and Myrick,[6] we find that its value increases considerably above a concentration corresponding to equal parts by weight of sugar and water, and hence the fluctuations can be expected to become smaller with increase in concentration of the solution. The density fluctuations also become smaller since the compressibility decreases with increasing concentration of the solution. As a result, the total fluctuations diminish, and hence there is less scattering at small angles, where the analogy with light-scattering can hold good. This is just what we find when the concentration increases beyond 1 : 1 by weight in all the sugar solutions

[5] C. V. Raman, Phil. Mag., 47, 671 (1924).

[6] Frazer and Myrick, J. Amer. Chem. Soc., 38, 1917 (1916).

examined. The appearance of a clear region round the central spot supports these conclusions and the general applicability of the theory of fluctuations to small angles of scattering in the case of X-rays.

X-ray diffraction of a number of liquids at different temperatures has been studied recently in the light of Raman and Ramanathan's theory.[7] On heating a liquid, the mean distance between the molecules increases, and hence the position of maximum intensity shifts towards the centre. Moreover, its compressibility also increases and the ring becomes broad and diffuse, as predicted by theory. When a liquid is heated in a closed tube it exerts a pressure on the walls of the tube, depending on the temperature. In a similar way canesugar exerts its osmotic pressure when dissolved in water, depending on the concentration. There is in fact a close analogy between the two phenomena, and what takes place with increase of temperature in the one case, can be brought about by suitable dilution in the other. So we find that when canesugar is dissolved in the smallest quantity of water, the water molecules are distributed inside like a gas, and give rise to a feeble general halation, while the sugar ring contracts, broadens and becomes diffuse at the edges, as in a liquid heated to a moderate temperature. The ring contracts further when the solution is diluted a little more ; but, when a concentration of about 1 : 1 is reached, there is a greater amount of randomness of distribution of the molecules, and the ring joins up with the centre. This corresponds to the critical state of the liquid where such a phenomenon might occur, though it has not yet been investigated. With more dilute solutions, the pattern is simply that for a compressed gas or vapour, taking into consideration the size of the molecule in computing the intensity of scattering. In fact, if a vapour or gas having the same molecular dimensions as canesugar

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[7] Ramasubramaniam, Ind. Jour. Phys., 3, i, 137 (1928).

($C_{12}H_{22}O_{11}$) or levulose ($C_6H_{12}O_6$), and occupying the same volume as that of the solution, were compressed to the extent given by the osmotic pressure exerted by the solution, it is natural to expect that it would show a pattern identical with that given by the sugar molecules in solution.

Thus we see that the theory of Raman and Ramanathan helps us to understand the nature of solutions as well. Another very important generalisation regarding the actual size of the dissolved molecule arises when the inner coronae of the dilute solutions of the sugars are examined in detail.

In a crystal powder, as is well-known, there is practically no scattering at small angles. When a very small quantity of water is added to sugar, the intermolecular distance increases and the ring contracts. We know that when there is a definite arrangement of molecules in a liquid, there would be destructive interference at small angles of scattering.[8, 9] This is the case in a solution up to a concentration of about 2:1. At the next dilution (1:1), the inner ring joins up with the central spot, and gives a fairly uniform halation. It is no longer admissible to expect any definite arrangement of the molecules in this dilute solution, and one can expect a fairly random distribution. There is no correlation between the phases of the scattered waves, and hence they add up just as in the gaseous scattering, the extent of which is limited by the size of the dissolved molecule. In fact, it can be seen easily that if the molecules be distributed at random, their distance apart can vary from the dimensions of the molecule up to a very large value. Hence from a measurement of the outer edge of the gaseous scattering, by applying the Bragg formula

$$a = \frac{\lambda}{2 \sin \frac{\theta}{2}}$$

[8] Raman and Ramanathan, *loc. cit.*
[9] Debye, Phys. Zeit., 28, 135 (1927).

one can get the value for the size of the dissolved molecule. The dilute solutions also should show this limit, but the edges will be fainter since the number of scattering molecules becomes less. When this limit is measured carefully, it is found that it agrees fairly well with the size of the molecule calculated from its mass and density. The results were however somewhat higher than the theoretical, which could be explained in either of two ways—(1) as due to the non-sphericity of the molecule, (2) as due to the water of hydration. If the molecule really attaches to itself five or six molecules of water, it is easy to see that higher values for the intermolecular distance will be obtained. However, before deciding this point, the photographs should be carefully microphotometered. A more quantitative study of these effects will form the subject of a future communication.

As already mentioned, the value for the outer limit of the corona should be taken when the ring has just joined with the central spot. If more dilute solutions are employed, longer exposures should be given to bring out the extent of the corona. The following table gives the dilutions, and the maximum extent of the corona for the different solutions, as well as the calculated size of the molecules.

<div align="center">TABLE I</div>

Solution	θ in degrees	λ in A.U.	$\sqrt[3]{\dfrac{m}{d}}$ in A.U.
Canesugar, 1 : 1	11·4	7·73	7·10
Levulose, 1 : 1	15·1	5·86	5·64
Glucose, 1 : 1	15·1	5·86	5·79

The intensity of the gaseous scattering depends on the number of scattering electrons in the molecule, and hence the bigger the molecule, the greater the intensity of scattering. In equivalent solutions of cane-sugar (e.g., 1 : 1 by

CANE SUGAR, SOLID

SOLUTION SUPERCOOLED

SOLUTION, 2 : 1

SOLUTION, 1 : 1

SOLUTION, 1 : 2

SOLUTION, 1 : 4

X-Ray Diffraction by Cane-Sugar Solutions
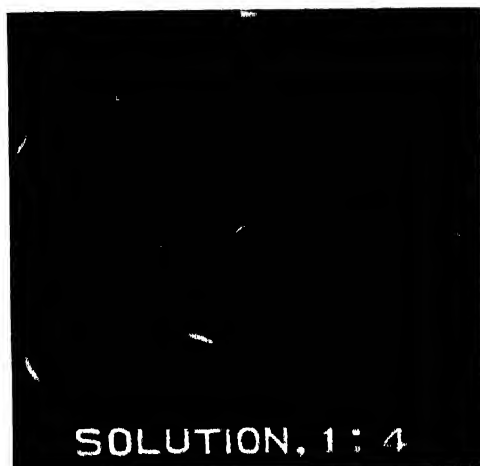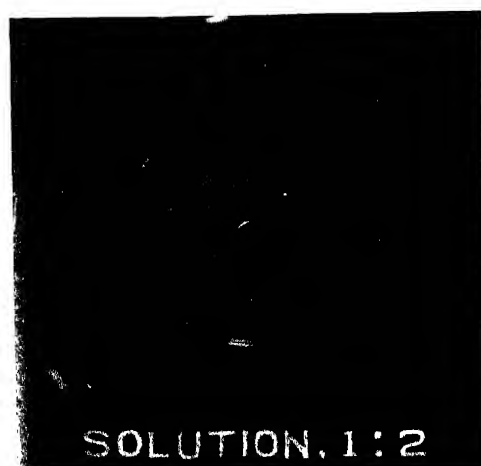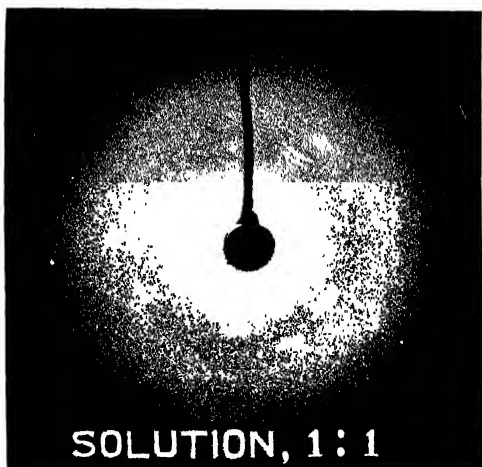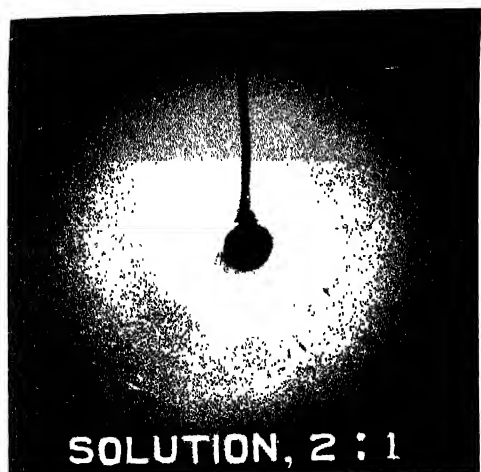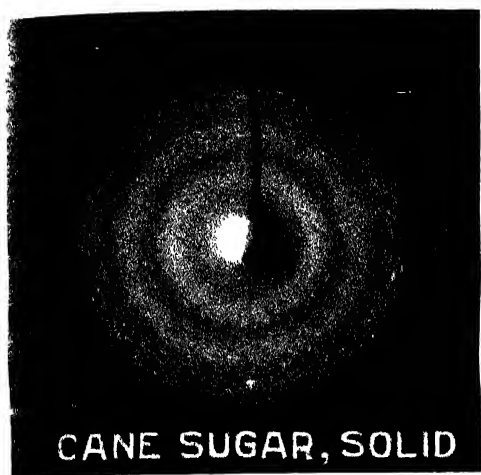
weight) as compared with levulose and glucose, it is found that in the former, the scattering is limited to a smaller area in the centre on account of the bigger size of the molecule and its intensity is greater than those in the latter, which extend over a larger area and hence are much weaker.

Glucose and levulose, both of the same formula $C_6H_{12}O_6$, show some essential differences in their patterns on dilution. In a 2 : 1 solution of levulose, the water ring appears very faintly at about 3.6 A.U., whereas in the case of glucose, the two rings have joined together producing a more or less uniform scattering up to about 3.5 A.U. In a 1 : 1 solution, the water ring is separated by a clear space from the inner ring in levulose, whereas in the case of glucose, this division is just perceptible and the outer ring is also slightly smaller. It is suggested that these differences might be connected with the fact that glucose can crystallise in the solid state with one molecule of water of crystallisation, and hence could be expected to have water molecules attached to it even in solution.

Experimental.

The apparatus used in this investigation was essentially the same as that described in the previous communications.[10] The X-ray tube was fitted with a copper anticathode, and was worked by an oil-immersed transformer at about 40 K.V. The window out of which the X-rays emerged consisted of very thin aluminium foil coated on the outside with rubber solution. The current in the tube was kept at 5—6 milliamperes and the exposures given ranged from $1\frac{1}{2}$ to 2 hours.

A circular brass disc with a hole in the centre, heavily gilded, and held between two other similar plates served

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[10] Krishnamurti, Ind. Jour. Phys., 2, iv, 498 (1928).

to hold the liquids examined. The thickness of the disc was 1 mm. Thin mica was used as windows as in the previous experiments, since it gave rise to spots only, and did not produce any ring of its own. Rubber solution was used to paste the mica to the cell. The distance between the cell and the photographic plate was 4·45 cms. A lead disc suspended by a stiff wire just in front of the plate served to cut off the direct beam.

For the powder photographs, the dry substance was powdered as finely as possible in an agate mortar. The following procedure was followed in preparing the solutions:

Canesugar solutions: Ordinary pure, white sugar crystals were used. A supercooled solution was prepared by weighing out the finely-powdered sugar and pure distilled water in the proportion of about 3:1, warming cautiously until a clear solution resulted, and suddenly cooling. The liquid in the cell was examined again after the exposure to make sure that no crystals had formed. The other solutions were prepared in a similar way and filtered before putting into the cell, the first portions of the filtrate being rejected.

Levulose solutions: Merck's extra pure variety of levulose was used. The procedure was the same as described above. All the solutions were filtered before use.

Glucose solutions: Merck's pure specimen of glucose was used. In this case, the maximum concentration which could be obtained was 2:1. This, as well as the next one (1·5:1) were kept at about 50°C. during the exposures, to prevent them from crystallising. The other solutions were prepared in the same way as described for canesugar.

The exposures given in all these cases ranged from $1\frac{1}{2}$ to 2 hours. The Lumiére extra rapid plates were used throughout to facilitate comparison. Freshly-distilled water which was examined under the same conditions did not show any marked scattering at small angles to the primary beam. The results obtained are set forth in the following tables.

PLATE X

LEVULOSE, SOLID

SOLUTION, 3 : 1

SOLUTION, 2 : 1

SOLUTION, 1 : 1

SOLUTION, 1 : 2

WATER.
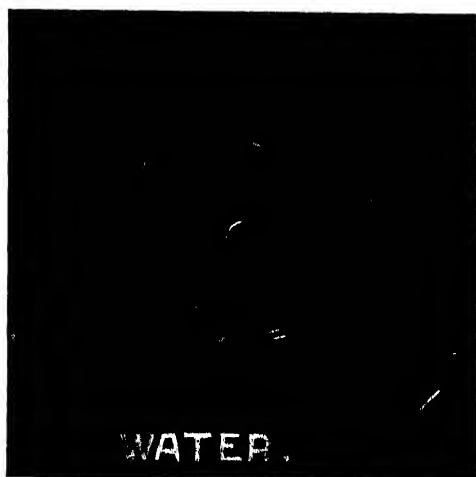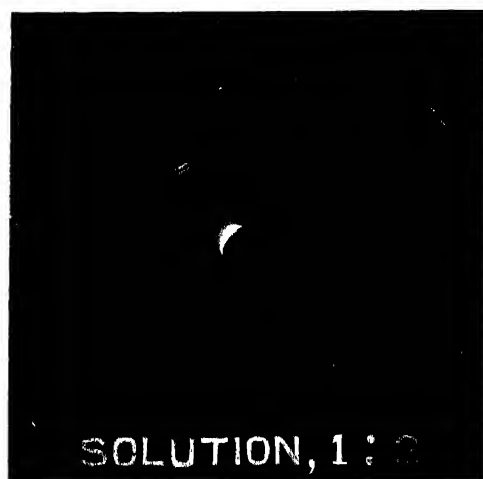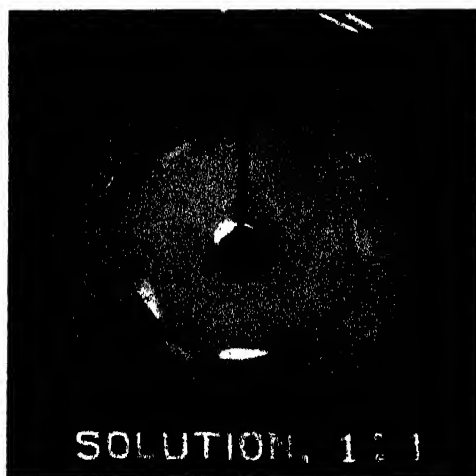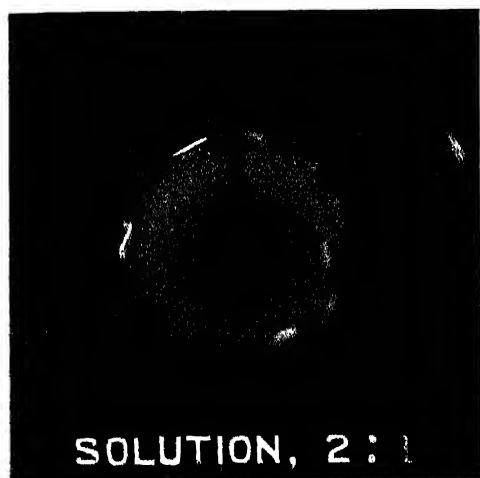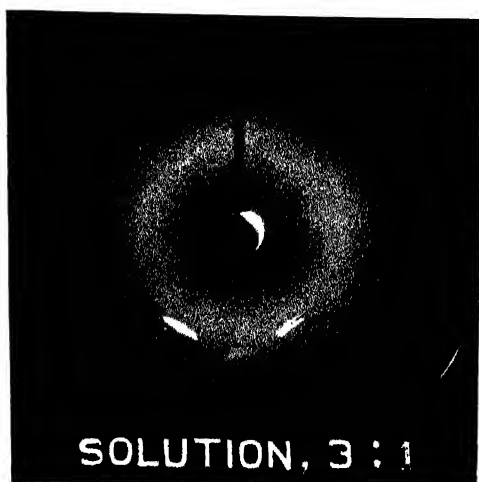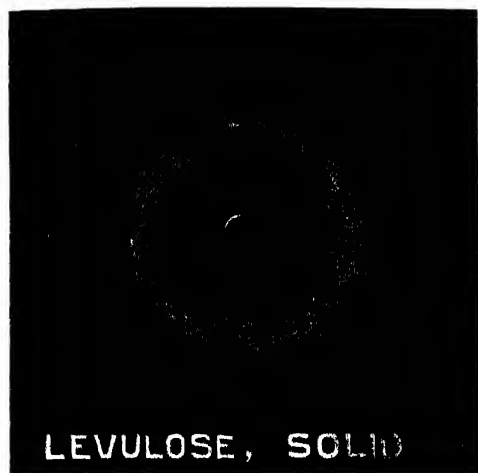
X-Ray Diffraction by Levulose Solutions

TABLE IIa

$\lambda = 1\cdot54$ A.U.

Canesugar Powder

	Inner margin.	Outer margin.	θ_1 in degrees.	λ_1 in A.U.	Intensity.
1	$10\cdot8°$	$13\cdot9°$	$12\cdot2$	$7\cdot27$	Strong.
2	$17\cdot2$	$20\cdot9$	$19\cdot2$	$4\cdot62$	,,
3	$23\cdot1$	$26\cdot8$	$24\cdot7$	$3\cdot59$	Med. strong.
4	...	...	$31\cdot7$	$2\cdot82$	Weak.
5	...	...	$38\cdot8$	$2\cdot32$	,,
6	...	...	...	...	Very weak.
7	...	...	...	...	,,

TABLE IIb

Canesugar Solutions

	Inner Ring.				Outer Ring.			
Concen-tration.	Inner limit.	Outer limit.	θ_1 in degrees.	λ_1 in A.U.	Inner limit.	Outer limit.	θ_2 in degrees.	λ_2 in A.U.
3 : 1	$9\cdot6°$	$13\cdot9°$	$11\cdot8$	$7\cdot51$	$18\cdot6°$	$24\cdot7°$	$20\cdot1$	$4\cdot42$
2 : 1	$8\cdot3$	$13\cdot0$	$10\cdot3$	$8\cdot56$	$19\cdot2$	$25\cdot3$	$22\cdot0$	$4\cdot03$
1 : 1	...	...	up to $11\cdot4$	$7\cdot73$	$19\cdot2$	$29\cdot1$	$24\cdot2$	3.67
1 : 2	...	...	$10\cdot2$ $\}$ $11\cdot4$	$8\cdot66*$ $\}$ $7\cdot73$	$22\cdot0$	$29\cdot3$	$25\cdot8$	$3\cdot45$
1 : 4	...	...	$8\cdot3$ $\}$ $11\cdot4$	$10\cdot63$ $\}$ $7\cdot73$	$22\cdot6$	$29\cdot8$	$26\cdot6$	$3\cdot35$
Water	...	...	...	...	$23\cdot7$	$30\cdot3$	$27\cdot3$	$3\cdot26$

* Wherever two values are given, one refers to the outermost edge and the other to where the intensity begins to fall off.

TABLE IIIa
Levulose Powder

	Inner margin.	Outer margin.	θ_1 in degrees.	λ_1 in A. U.	Intensity.
1	15·7°	19·5°	18·1	4·91	Strong.
2	...	...	29·3	3·04	Med. strong.
3	...	...	35·7	2·51	Weak.
4	...	...	41·2	2·19	,,

TABLE IIIb
Levulose Solutions

	Inner Ring.				Outer Ring.			
Concentration.	Inner limit.	Outer limit.	θ_1 in degrees.	λ_1 in A. U.	Inner limit.	Outer limit.	θ_2 in degrees.	λ_2 in A.U.
3:1	13·3°	18·3°	15·7	5·64	...	...	...	...
2:1	12·1	17·8	14·8	5·98	...	...	about 24·7	3·60
1:1	...	...	up to 15·1	5·86	23·7°	28·3°	25·3	3·52
1:2	...	...	13·3 } 15·1 }	6·65 } 5·86 }	23·7	29·3	25·8	3·45
1:4	...	...	11·4 } 15·1 }	7·73 } 5·86 }	23·7	29·8	26·8	3·32
Water.	...	...	...	...	23·7	30·3	27·3	3·26

TABLE IVa
Glucose Powder

	Inner margin.	Outer margin.	θ_1 in degrees.	λ_1 in A.U.	Intensity.
1	5·8°	14·5°	10·2	8·66	Weak
2	18·1	22·3	20·3	4·36	Strong
3	...	...	24·2	3·67	Weak
4	...	...	26·8	3·32	,,
5	...	...	29·3	3·04	Very weak
6	...	...	36·1	2·48	,,
7	...	...	41·2	2·18	,,

GLUCOSE SOLID

SOLUTION, 2 : 1

SOLUTION, 1 : 1

SOLUTION, 1 : 2

SOLUTION, 1 : 4

WATER.

X-Ray Diffraction by Glucose Solutions
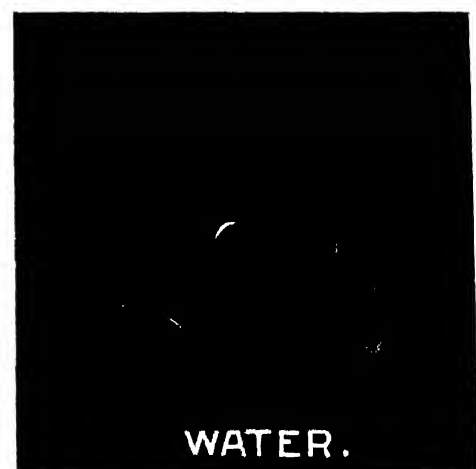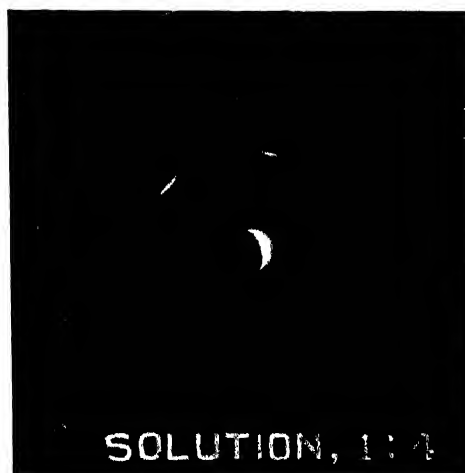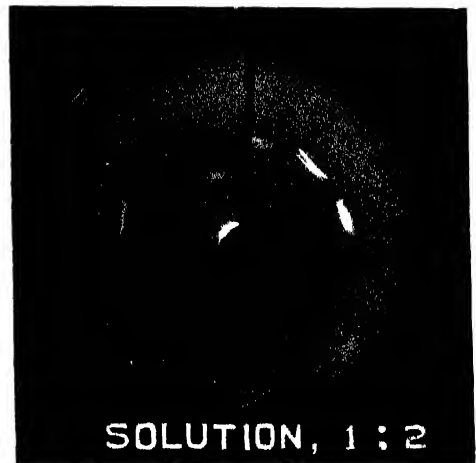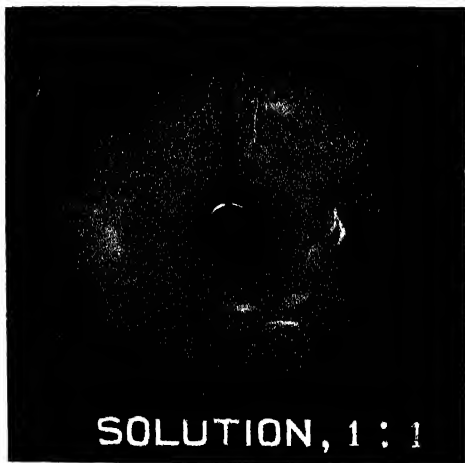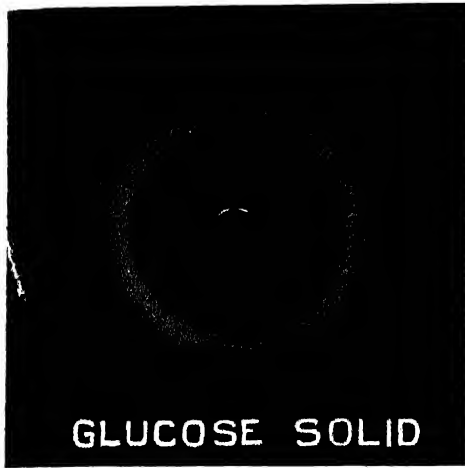
TABLE IV*b*

Glucose Solutions

| | Inner Ring. | | | | Outer Ring. | | | |
Concentration.	Inner limit.	Outer limit.	θ_1 in degrees.	λ_1 in A. U.	Inner limit.	Outer limit.	θ_2 in degrees.	λ_2 in A. U.
2:1	12·7°	25·3°	16·3	5·43	..	..	...	upto 3·50
1·5:1	..	..	13·9	6·37	...	...	22·0	4·03
1:1	...	..	up to 16·1	5·86	21·5°	26·8°	23·7	3·75
1:2	...	...	13·3 } 15·1 }	6·65 } 5·86 }	22·6	28·8	26·3	3·38
1:4*	..	..	about 11 1	7·04	23·7	29·3	26·8	3·32
Water	...	..	...	...	23·7	30·3	27·3	3·26

Investigations are in progress to elucidate the nature of colloidal solutions, soap solutions, and the different kinds of electrolytes and non-electrolytes not examined before. The case of the solution of an organic substance possessing a simple cubic lattice in the solid state is of great theoretical interest. Such a substance has been found in hexamethylene tetramine.[11] So far examined, the substances which crystallise with water of crystallisation have different X-ray patterns in solutions, and it is proposed to study the effects, some of which have been dealt with in this paper, more fully.

I take this opportunity of thanking Prof. C. V. Raman, F. R. S., for the keen interest which he took in this investigation, and for his valuable suggestions during its progress.

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* A weak negative.

[11] Dickinson and Raymond, J. Amer. Chem. Soc., 45, 22 (1923).

10

X-ray Diffraction of Crystal Powders and Liquids in Relation to their Constitution

BY

P. KRISHNAMURTI.

(Plates XII and XIII.)

ABSTRACT.

A number of organic liquids have been examined to correlate their constitution with their X-ray diffraction patterns The ortho disubstituted benzene derivatives showed the presence of two rings and para compounds of only one, as shown previously (Krishnamurti, *Ind. Jour. Phys.*, 2, iii, 355, 1928). *n*-Butyl benzoate showed a very faint inner ring in approximately the same position as in the salicylate. Geraniol and terpineol showed some differences, the former giving a broader and more diffuse halo while the latter gave a clearly defined one. The inner ring due to double molecular spacing (being alcohols and hence associated) was smaller in the case of geraniol than in terpineol, showing that the former consisted of longer molecules. Some benzene derivatives with a long side-chain gave rings of about the same size as in a long chain aliphatic derivative like oleic acid.

Some ortho disubstituted compounds and one meta and one para compound were examined both in the powder and liquid states. The liquid patterns in the ortho and meta compounds showed the two rings present in the powder pattern, the outer one having contracted, and the inner one of practically the same size. The rings were broader and more diffuse at the edges in the liquids. The para compound showed a number of rings close together in the powder, which in the liquid joined

together into one broad ring. The faint outer rings in the solid gave place to a general halation in the liquid.

An explanation for the presence of two separate rings in the ortho and meta compounds is offered, the outer ring as due to the thickness of the molecule, and the inner to its length and breadth. This is supported by the fact that in the ortho compounds, the outer spacing increases very slowly with an increase in size and length of the substituting groups, whereas the inner spacing alters very rapidly. The clear separation of the rings is due to the orientative influence of the molecules on one another. In the para compound, just as in the long-chain aliphatic liquids, only the spacing due to the average thickness of the molecules is obtained. The changes in the diffraction patterns when passing from the solid to the liquid state, e.g., the contraction and diffuseness of the ring as well as the increase of scattering at small angles are discussed in the light of the theory of Raman and Ramanathan.

Theoretical.

In a previous communication,[1] it was shown that in disubstituted benzene derivatives, the ortho and meta compounds produced two separate diffraction rings, whereas the para compounds gave rise to a single ring only. The present investigation includes some more substances of this type, a study of which is likely to throw some light on the origin of these double rings. Since our present knowledge of the X-ray diffraction effects in the solid crystalline state[2] is fairly definite, it was thought that an examination of the ortho and meta compounds both in the solid and liquid states would eventually lead to the correct explanation of the effects in the latter. Many organic substances have been examined by other investigators in the solid and liquid states,[3, 4] and it has been found that in almost all cases the ring in the liquids appears in approximately the same

[1] Krishnamurti, Ind. Jour. Phys., 2, iii, 355 (1928)
[2] Bragg, X-rays and crystal structure (Bell & Sons, 1924).
[3] Herzog and Jancke, Zeit. fur Phys. 45, 194-99 (1927).
[4] Broome, Phys. Zeit., March, 1923, Plate VI.

ETHYL PHTHALATE

P – CYMENE

N-BUTYL SALICYLATE

N – BUTYL BENZOATE

GERANIOL

TERPINEOL

X=Ray Diffraction by Liquids
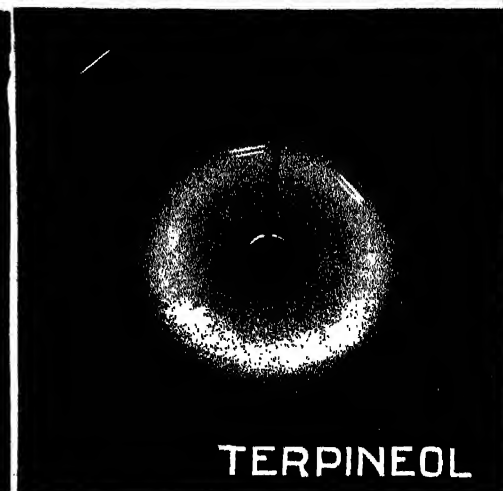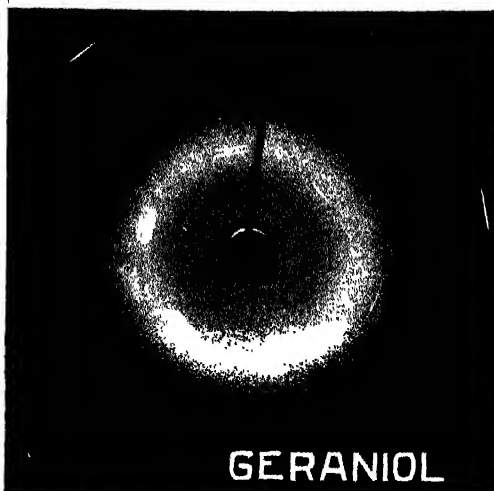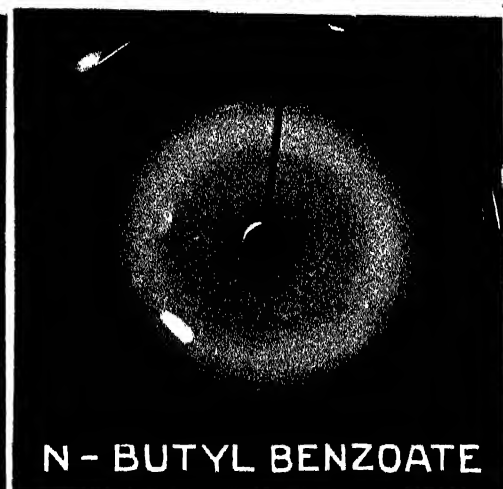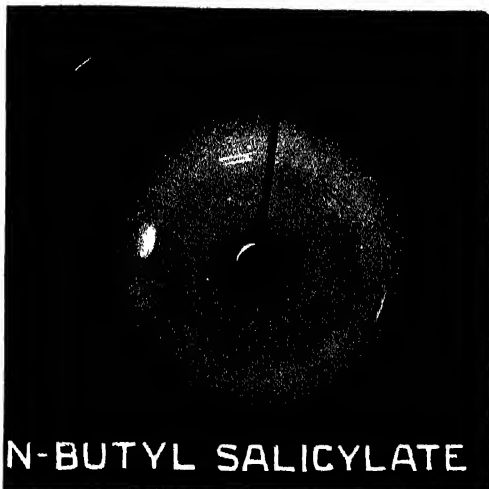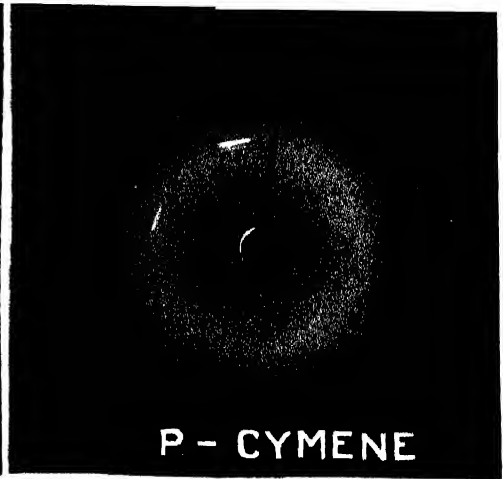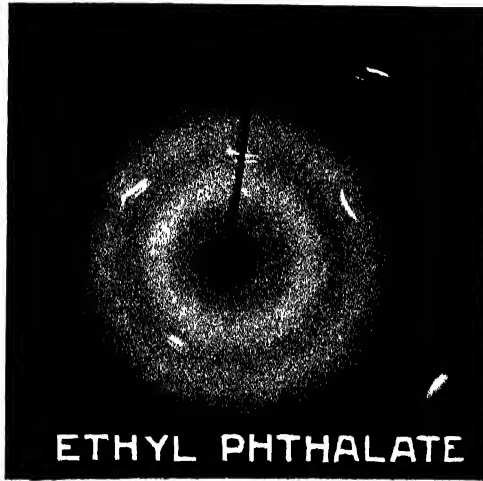
position as the most prominent ring or groups of rings in the solid when examined by the powder method.

In the present investigation, some more ortho disubstituted benzene derivatives have been examined in the liquid state, and all of them invariably showed the presence of two prominent rings. The intensity of the outer ring with respect to the inner ring increases in the following order :

(1) Ethyl o-phthalate ... both rings equally strong.
(2) o-nitraniline ... „
(3) o-nitro phenol ... „
(4) n-butyl salicylate ... outer ring stronger than the inner.

Among para compounds, p-cymene showed the presence of only one prominent ring.

On comparing salicylaldehyde, methyl salicylate and n-butyl salicylate, we find that with increasing length of the side-chain, both the inner and outer rings have contracted. We also find that the outer ring increases in brightness when compared with the inner, in the order given above, which is also the order of increasing size of the substituent groups. Comparing next the esters of benzoic acid, the methyl, ethyl and n-butyl benzoates, the inner ring which could hardly be observed in the first two, appears with increased brightness in n-butyl benzoate. The size of this faint inner ring decreases in the order given, while the size of the main outer ring contracts from methyl to ethyl benzoate, and remains fairly constant in size with further increase in the length of the chain. The size of the ring is then similar to that of a long-chain aliphatic derivative, e.g., oleic acid. Benzyl acetate, too, with a long side-chain attached to the benzene ring shows the same size of the outer ring. The following table shows these relations clearly :

TABLE I.

Liquid.	λ_1 in A.U.	λ_2 in A.U.	Intensity.
Salicylaldehyde ...	5·47	3 56	1 > 2
Methyl salicylate ...	6·65	3·78	1 = 2
n-Butyl salicylate ...	9·24	4·36	1 < 2
Methyl benzoate ...	5·75	4·24	1 very faint
Ethyl benzoate ...	6·65	4·46	,,
n-Butyl benzoate ...	9·24	4·48	1 faint
Benzyl acetate ...	...	4·62	...
Oleic acid ...	...	4·62	1 diffuse

n-Butyl benzoate and n-butyl salicylate were examined to find out the influence of the hydroxyl group in the ortho position to a long n-butyl group. The salicylate as expected, shows two fairly intense rings. The benzoate also shows a very faint ring almost in the same position as in the salicylate. The outer ring is broader in the salicylate than in the benzoate.

There is only one way of explaining all the above observations regarding the origin of the two rings produced by the ortho compounds. Raman and Ramanathan [1] have shown from first principles that the peak in the diffraction halo of liquids occurs at a wavelength equal to the mean distance between neighbouring molecules. They have also pointed out that in the case of highly asymmetric molecules in which we might have two or even three values for the mean distance between neighbouring molecules depending on their relative configuration, there would be one spacing for the longest distance of approach of the molecules, and another for the shortest. Evidently, one spacing depends on the length and breadth of the molecule while the other depends on its thickness. In the case of benzene, since there are no polar groups to give it

Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., 8, ii, 154 (1923).

a definite orientation in any direction, the scattering takes place between the two limits mentioned above. On the other hand, in the case of oleic acid, the molecules exert an orientating influence on each other, with the result that one ring is produced by the thickness of the molecule,[1] and the other round the central spot due to the length of the molecule. This latter spacing is very faint since it occurs less frequently than the other.

In the case of the ortho and meta disubstituted compounds, each molecule exerts orientating influence on the other, since the substituting groups are mostly polar. Since the molecules are thus held firmly in their positions, it is quite natural to expect that the main spacings of the crystal would persist in the state of the liquid, and this has actually been found to be the case in the ortho and meta disubstituted benzene derivatives. Of the two spacings which correspond to the two main rings produced in the ortho and meta compounds in the liquid state, one should be evidently due to the thickness and the other to the length and breadth of the molecule. These should be separated from each other by a fairly clear region, since the molecules cannot assume different orientations as has been pointed above. The para substituted compounds, on the other hand, resemble the long-chain aliphatic compounds since the molecules are fairly long, and it is the thickness which will give the most prominent spacing. The molecules will tend to adjust themselves parallel to one another, and hence only one ring will result depending on this distance between the molecules.

On the basis of the above discussion it is easy to explain the changes in the size and intensity of the rings produced by the disubstituted benzene derivatives. In the first instance, the spacings for the outer rings are similar for a variety of ortho compounds, being approximately 3·5 A.U. This can be

[1] Sogani, Ind. Jour. Phys., 2, i, 115 (1927).

considered as due to the average thickness of the molecule. The inner ring ought then to represent the average length of the molecule. It can be seen by a review of the existing data that the larger the size of the substituting groups, the larger the spacing of the inner ring. In fact, when the substituent group is very long as in *n*-butyl salicylate the inner ring is very small and the molecular spacing correspondingly large.

TABLE II.

Liquid.	λ_1 in A.U.	λ_2 in A.U.	Intensity.
O-Toluidine ...	5·06	3·35	1 > 2
Salicylaldehyde ...	5·47	3·56	1 > 2
O-Nitrobenzaldehyde ..	6·37	3·56	1 = 2
Methyl Salicylate ...	6·65	3·78	1 = 2
Ethyl phthalate ...	7·00	4·14	1 = 2
n-Butyl salicylate ...	9·24	4·36	1 < 2

It will be seen that the thickness of the molecule also increases with an increase in length of the substituent groups.

R egarding the intensities of the two rings, it can be expected that the spacings which occur most and those which are caused by the interference of the waves from the largest number of electrons will be the stronger spacings. Since the outer ring increases in brightness with the increasing length and size of the substituent groups, it can be inferred that the longer spacing occur less frequently than the shorter one due to the thickness of the molecule.

The two liquids geraniol and terpineol were examined to find out the changes in the X-ray pattern when an openchain compound is converted by certain reagents into a closed-chain compound of the same formula.

GERANIOL

$$\begin{array}{c} CH_3 \\ CH_3 \end{array} \Big\rangle C = CH-CH_2-CH_2-C=CH-CH_2OH$$

CH₃

$$\begin{array}{c} CH_3 \\ CH_3 \end{array} \Big\rangle C-CH \Big\langle \begin{array}{c} CH_2-CH_2 \\ CH_2 -CH \end{array} \Big\rangle C-CH_3$$

OH
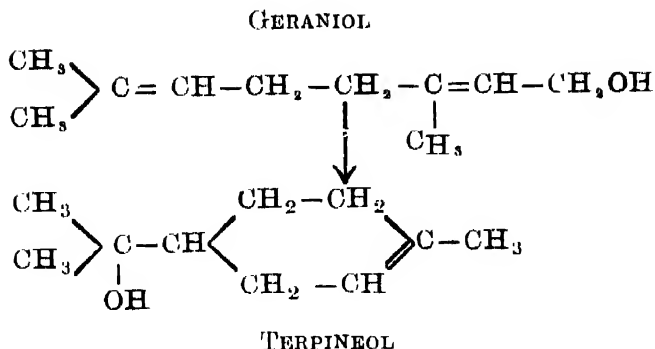
TERPINEOL

Geraniol is a long-chain alcohol which is converted into the isomeric terpineol by the action of acetic acid to which $1-2\%$ sulphuric acid is added. Geraniol gives a halo which is broad and diffuse like that of hexane. Being also an alcohol and hence associated, the inner faint ring appears which is however very small showing that the molecule is correspondingly very long. There is also a general scattering outside the principal halo. But in the case of terpineol, the main ring is very sharp just like the halo for benzene, and is smaller than that of geraniol. The inner ring is also larger in this case showing that the spacing due to the double molecules has decreased on account of ring formation.

Diphenylmethane and diphenylamine show characteristic differences in their patterns. While the main outer rings are practically identical, and the scattering outside the halo of the same order of intensity in both cases, in the case of diphenylamine the faint inner ring which has been explained as due to molecular association [1] is present, while in diphenylmethane it is entirely absent and the inner region is quite clear, showing that the latter is very little associated.

The changes in the diffraction pattern when a crystalline solid melts and changes into a liquid have been investigated for some ortho, meta and para compounds. It is found that in all cases the most prominent rings in the powder pattern

[1] Krishnamurti, Ind. Jour. Phys., 2, iv, 491 (1928).

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persist also in the liquid state undergoing a slight decrease in size. The fainter rings in the solid appear as a general halation in the corresponding area of the liquid. There is also a contraction of the principal ring when passing from the solid to the liquid state. The ortho and meta compounds differ from the para in the following respect. In the former, only two prominent rings appear in the pattern for the powder, which persist in the liquid state also, the outer one with a slight contraction in size, and the inner one with practically no contraction. The rings for the liquids are also broader and more diffuse at the edges than in the solids. In the para compounds, however, a number of prominent rings are observed, lying close together, which, in the liquid give place to one strong broad ring corresponding to the most prominent one in the solid, with considerable scattering both on the outside and inside of this halo. All these features are observed in o-nitrobenzaldehyde, o-nitrophenol, o-nitraniline, m-nitro benzaldehyde [1] and p-toluidine. The para compounds show an analogy with a mono-substituted derivative like acetophenone-oxime. The case of diphenylamine is also similar to the above, and this being a polar compound, the ring due to the long spacing appears in the liquid also.[2] Acetamide, an aliphatic derivative, shows two rings in the solid state which are also shown in the liquid state, though both of them have decreased in size. This is similar to the cases of acetic acid and lauryl alcohol.[3]

These facts evidently show that some at least of the crystal planes remain intact, though considerably modified, when passing from the crystalline to the liquid state. It is well-known that very finely-divided powders give diffraction rings which are fairly diffuse. If the crystal fragments could be subdivided further and further, the rings will

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[1] For the liquid picture, see Ind. Jour. Phys., Plate VIII (1928).

[2] For liquid picture, see Ind. Jour. Phys., Plate XVIII (1928).

[3] Sogani, *loc. cit.* Also Stewart and Morrow, Phys. Rev., 30, 240 (1927).

become more diffuse, and finally some of the less intense rings will appear only as a general scattering, while, if the prominent rings are near together, they would join up and give one broad ring. If we can imagine the powder to be so finely-divided that only molecules are present even then thermodynamic considerations would secure a certain degree of uniformity of the molecular spacing. Hence, in a liquid, it is natural to expect that the less prominent details present in the powder would disappear and only the main rings would persist, though undergoing some contraction and diffuseness. The contraction of the ring can be explained as due to the volume change which takes place during the transition from the solid to the liquid state. The diffuseness and spreading out of the ring is due to the increased compressibility of the liquid. We find from the formula given by Raman and Ramanathan [1] that the intensity of scattering is proportional to its isothermal compressibility. In a crystal powder, where the compressibility is very small, the fluctuations of density are also very small and hence we find very little scattering at small angles to the primary beam where the analogy with light-scattering holds good. But in a liquid, due to the increase in compressibility, we find a greater amount of scattering at small angles, as well as on the outer and inner margins of the halo. In addition, we find in the case of polar substances, another fainter ring in the liquid which has been explained as due to the bimolecular spacing.[2]

It may be useful to compare the known positions of the atoms and layers of atoms in diamond and graphite, and see what comparison can be drawn with reference to the bonds between the molecules in a liquid. The distance between each pair of carbon atoms is 1·54 A. U. in diamond and 1·50 A. U. in graphite and the distance

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[1] Raman and Ramanathan, *loc. cit.*

[2] Krishnamurti, *loc. cit.*

between the two successive layers 2·05 and 3·41 A. U. respectively. A carbon atom in graphite in one layer s equidistant from its three nearest neighbours in the next layer, being 3·25 A.U. The bonds between one layer and the next are greatly weakened in graphite, and in consequence, the layers slide over each other easily, giving it good lubricating properties. But the bonds between atoms in the same layer are almost as strong as in diamond. It can be imagined that a similar change takes place when a crystalline solid melts and assumes the liquid state. The bonds between the successive layers are greatly weakened, and hence it is able to assume any shape. The weakness of the bonds between the molecules is shown by the low melting points of the organic crystals. Since the forces which bind together the atoms in the molecule are preserved, the molecule retains its identity.

From the work of Bragg [1] on the crystal structures of benzene, naphthalene and anthracene, it is almost certain that the molecules possess a thickness of about 3·00 A.U. at right angles to the plane of the ring. The following diagrams of benzene and naphthalene taken from a recent paper by E. Mack, Jr.[2] show the dimensions of the molecules in A. U.
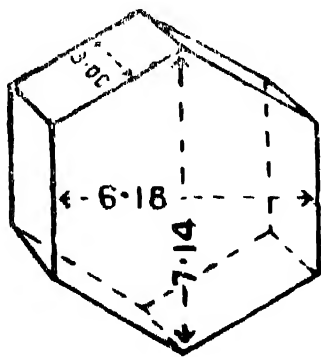
BENZENE   NAPHTHALENE
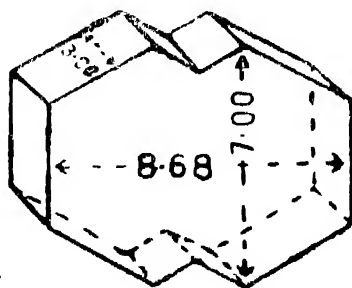
Bragg, *loc. cit.*   [2] Mack, Jr., J. Amer. Chem. Soc., 47, 2468 (1925).

O - NITRO BENZALDEHYDE (POWDER)

O - NITRO BENZALDEHYDE (LIQUID)

O - NITRO PHENOL (POWDER)

O - NITRO PHENOL (LIQUID)

NITRO BENZALDEHYDE (POWDER)

DIPHENYLAMINE (POWDER)
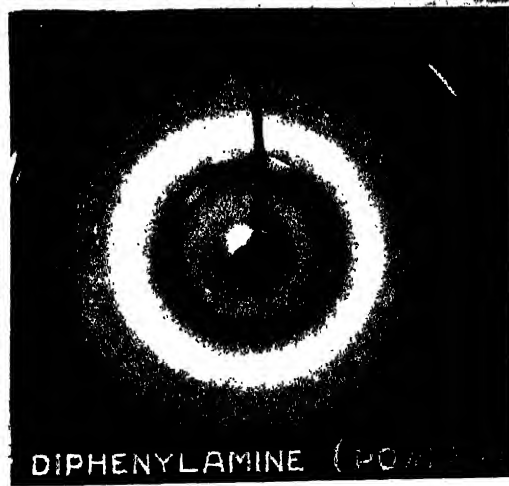
X=Ray Diffraction in Solid and Liquid States

Thus the thickness of the benzene ring has a constant value of 3·00 A. U. frcm Bragg's measurements, which agree with those of Mack from diffusion experiments. We find that according to the results set forth in Tables I and II, the spacing of the outer ring in many of the ortho compounds is approximately 3·5 A. U. a value closely corresponding to Bragg's value of 3·00 for the thickness of the benzene ring, considering the changes in volume which take place on melting. The effective thickness can also be seen to vary with the nature of the substituents, a maximum of 4·36 A. U. being obtained for n-butyl salicylate. This value lies between 3·00 for the thickness of the benzene ring, and 4·62 A. U. obtained for the thickness in the case of a long-chain aliphatic compound, oleic acid. This shows that the outer ring is most probably due to the thickness of the molecule, as pointed out already. The inner ring is evidently due to the length of the molecule since the spacing increases with the length of the molecule. In the case of polar compounds, this spacing is due to the length of two molecules, probably joined together end to end.

Experimental.

The same apparatus and experimental procedure was adopted as described in a previous communication.[1] The X-ray tube was worked by a transformer at about 40 K.V., and a current of 5-6 milliamperes in the tube was obtained steadily. The exposures ranged from 1½- 2 hours in all cases.

The cell was a heavily-gilded brass disc with a hole in the centre to hold the liquid examined. Thin mica windows

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[1] Krishnamurti, *loc. cit.*

were used which were attached to the cell with ordinary gum solution. A lead disc in front of the photographic plate served to cut off the direct beam in some cases.

The substances used were those supplied by Kahlbaum, Merck or the B. D. H. For the powder photographs, the substances were ground as finely as possible in an agate mortar, and pressed into the cell. No mica was used in these cases unless the substances happened to be hygroscopic. The liquid patterns for the solid substances were obtained by keeping them just above their melting points during the exposures. The angles of scattering were calculated from the radius of the halo measured from the negatives visually, and the spacings calculated from the formula :

$$\lambda_1 = \frac{1 \cdot 54}{2 \, \mathrm{Sin} \, \frac{\theta}{2}}$$

1·54 being the wavelength of Cu Kα radiation. The results are given in the following tables :

TABLE III.

Some Organic Liquids.

Liquid.	Formula.	θ_1 in degrees.	λ_1 in A. U.	θ_2 in degrees.	λ_2 in A. U.	$\sqrt[5]{\dfrac{m}{d}}$ in A. U.	Limits Inner Ring.	Limits Outer Ring.
(1) Ethyl o-phthalate	$C_6H_4 < \begin{array}{l} COOEt\ (1) \\ COOEt\ (2) \end{array}$	12.7	7·00	21·5	4·10	6·90	10·8°–14·5°	19·5°–23·4°
(2) n-Butyl salicylate	$C_6H_4 < \begin{array}{l} OH\ (1) \\ COO\text{-}n\text{-butyl}\ (2) \end{array}$	9·6	9·24	20·3	4·36	...	6·4–11·8	17·2–23·1
(3) n-Butyl benzoate	$C_6H_5.\ COO\text{-}n\text{-butyl}$	9·6	9·24	19·8	4·48	6·66	Faint	16·6–22·0
(4) p-cymene	$C_6H_4 < \begin{array}{l} CH_3\ (1) \\ C_3H_7\ (4) \end{array}$	...	...	17·2	5·16	6·38	...	14·5–19·5
(5) Geraniol	See *p.* 231	5·8	15·31	18·1	4·91	6·62	Faint	15·7–20·9
(6) Terpineol	,,	8·3	10·63	17·2	5·16	6·49	Faint	14·5–19·8
(7) Benzyl benzoate	$C_6H_5.\ CO.\ O.\ CH_2.\ C_6H_5$	...	...	19·2	4·62	6·81	...	16·0–21·5
(8) Diphenyl methane	$C_6H_5.\ CH_2.\ C_6H_5$	...	...	18·6	4·76	6·41	...	16·3–20·9
(9) Benzyl acetate	$C_6H_5.\ CH_2.\ O.\ CO.\ CH_3$	...	...	19·2	4·62	6·18	...	16·3–21·5
(10) Oleic acid	$CH_3.\ (CH_2)_{18}: CH.\ CH_2 : COOH$	...	...	19·2	4·62	8·05	...	16·3–21·7

TABLE IV.

Crystal Powder and Liquid Patterns.

Substance.	Formula.	θ_1 in degrees.	λ_1 in A.U.	θ_2 in degrees.	λ_2 in A.U.	$\sqrt[3]{\frac{m}{d}}$ in A.U.	Limits Inner Ring in degrees	Limits Outer Ring in degrees	REMARKS
(1) O-Nitro-benzalde-hyde ; solid	$C_6H_4 < \begin{array}{l} NO_2 \ (1) \\ CHO \ (2) \end{array}$	13·9	6·37	25·3	3·52	...	12·1–15·7	22·6–27·8	3rd ring present.
(2) ,, liq.		13·9	6·37	24·2	3·67	...	12·4–16·7	22·0–25·8	
(3) O-Nitro-phenol, solid	$C_6H_4 < \begin{array}{l} OH \ (1) \\ NO_2 \ (2) \end{array}$	14·8	6·02	26·8	3·32	...	12·4–16·3	24·5–29·3	
(4) ,, liquid.		14·5	6·10	24·5	3·63	5·42	12·4–16·0	22·3–26·8	
(5) O-Nitraniline, solid	$C_6H_4 < \begin{array}{l} NO_2 \ (1) \\ NH_2 \ (2) \end{array}$	14·5	6·10	26·8	3·32	...	12·4–16·6	22·3–29·3	Another ring present.
(6) ,, liquid		14·5	6·10	24·2	3·67	...	12·4–16·9	22·6–25·8	
(7) m-Nitro-benzalde-hyde, solid.	$C_6H_4 < \begin{array}{l} NO_2 \ (1) \\ CHO \ (3) \end{array}$	13·9	6·37	26·8	3·32	...	12·1–16·0	22·6–30·3	
(8) ,, liquid		14·0	6·32	22·8	3·90	...	12·6–16·8	22·8–27·2	

p-Toluidine, solid	$C_6H_4 <{}^{CH_3\,(1)}_{NH_2\,(4)}$	17·8	5·00	24·5	3·63	...	14·5–20·3	22·6–29·3 More rings present.
(0) ,, liquid		17·8	5·00	·	...	5·54	14·5–20·6	... Outer scattering.
(1) Acetophenone Oxime, solid	$C_6H_5.C-CH_3$ $\underline{N}OH$	11·4	7·73	21·2	4·19	...	9·6–13·6	18·1–24·2 3rd ring present
(2) ,, liquid		...	...	19·6	4·52	...	...	14·8–24·1
(3) Diphenylamine, solid	$C_6H_5.NH.C_6H_5$	8·9	9·88	19·5	4·54	6·23	6·4–10·8	16·9–21·5 3rd ring present
(4) ,, liquid		9·4	9·54	18·6	4·76	...	Faint	16·3–20·6 Outer scattering.
(5) Acetamide, solid	$CH_3.CO.NH_2$	15·1	5·86	24·7	3·60	...	12·7–16·9	22·0–27·1
(6) ,, liquid		10·8	8·17	20·3	4·36	4·39	Faint	18·6–23·7

It is hoped that a more quantitative study of the diffraction phenomena in pure liquids by finding out the distribution of intensity in the patterns from their microphotometered curves, would prove useful in developing a complete theory of liquid diffraction. This is being carried out, and the results will form the subject of another communication.

I wish to acknowledge my indebtedness to Prof. C. V. Raman, F.R.S., for his valuable suggestions and guidance during the course of this work.

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Thermodynamics of the Compton Effect with Reference to the Interior of the Stars

BY

S. Chandrasekhar.

Abstract.

This paper deals with the statistical equilibrium of a system containing (1) electrons and quanta and (2) electrons, ionised atoms and quanta. Expressions are derived for the ratio of the probability coefficients connected with the 'Compton-type' collisions and 'Reversed-Compton type' collisions. This is nearly unity in the first case and nearly 3.3×10^{27} in the second case. This enormous difference in the results in the two cases is explained as due to the fact that the Reversed Compton Effect in the case of bound electrons is one of a triple collision and that with free electrons is an ordinary double collision. On this basis, the softening of high frequency radiation created in the interior of a star is attributed to the Compton-scattering with bound electrons.

1.   Compton Scattering with Free Electrons.

Let a quantum of energy $h\nu(=E_2)$ collide with an electron of energy E_1. After the collision let the recoil electron go with energy E_3 and the scattered quantum with $E_4(=h\nu')$. If the collision is of the Compton-type the electron goes with increased energy and the quantum with reduced frequency

$$(i.e.) \quad h\nu > h\nu' \text{ and } E_3 > E_1$$

$$[\text{But} \quad h\nu + E_1 = h\nu' + E_3]$$

The probability of Compton collision can be determined by applying for the number of electrons the Fermi-Dirac statistics and for the number of quanta Bose's expression. The probability of Compton collision is evidently proportional to the numbers of each present. The probability of the Compton collision is

$$= a \times \frac{1}{h^3} \times 2\pi. \ (2m)^{\frac{3}{2}} E_1^{\frac{1}{2}} \frac{1}{e^{\alpha + \frac{E_1}{kT}} + 1} \ dE_1$$

$$\times \frac{1}{h^3} \times 2\pi \ (2m)^{\frac{3}{2}} E_2^{\frac{1}{2}} \frac{1}{e^{\frac{E_2}{kT}} - 1} \ dE_2 \qquad \ldots \ (1)$$

Consider the inverse process now. An electron with energy E_3 and a quantum with energy E_4 collide and after the collision the quantum gets hardened. The probability is

$$= a' . \ \frac{1}{h^3} \times 2\pi (2m)^{\frac{3}{2}} . \ E_4^{\frac{1}{2}} . \ \frac{1}{e^{\frac{E_4}{kT}} - 1} . \ dE_4$$

$$\times \frac{1}{h^3} \times 2\pi \ (2m)^{\frac{3}{2}} . \ E_3^{\frac{1}{2}} . \ \frac{1}{e^{\alpha + \frac{E_3}{kT}} + 1} . \ dE_3. \ \ldots \ (2)$$

These two according to the principle of detailed balancing should be equal if there is thermodynamic equilibrium. Equating the two expressions we get

$$\frac{a}{a'} = \sqrt{\frac{E_3 . E_4}{E_1 . E_2}} \ \frac{\left(e^{\frac{E_2}{kT}} - 1\right)\left(e^{\alpha + \frac{E_1}{kT}} + 1\right)}{\left(e^{\frac{E_4}{kT}} - 1\right)\left(e^{\alpha + \frac{E_3}{kT}} + 1\right)} .$$

If we are considering very hard quanta, and a system at very high temperature, we can, because the energy is conserved, write

$$\frac{a}{a'} = \sqrt{\frac{E_3 . E_4}{E_1 . E_2}} = \sqrt{\left(1 + \frac{\delta\nu}{E_1}\right)\left(1 - \frac{\delta\nu}{E_2}\right)}$$

where $\delta\nu =$ change in the frequency of the initial and the scattered quantum.

Now the change in the frequency of the scattered quantum after collision with a moving electron has been worked out by Dirac and he gives

$$\frac{\delta\nu}{\nu} = (4k\mathrm{T} - h\nu)/mc^2 \; (1 - \cos\theta')\,[1]$$

which is very small under the conditions of a Star's interior.

Hence $\frac{a}{a'}$ is nearly unity to a rough approximation.

If we write now

$$\mathrm{K} = a.\sqrt{\mathrm{E_1.E_2}}$$

$$\text{and } \mathrm{K} = a'.\sqrt{\mathrm{E_3 E_4}}$$

$$\text{and } n_1 = \frac{1}{e^{a + \frac{\mathrm{E_1}}{k\mathrm{T}}} + 1} \quad, n_2 = \frac{1}{e^{\frac{\mathrm{E_2}}{k\mathrm{T}}} - 1}$$

$$n_3 = \frac{1}{e^{a + \frac{\mathrm{E_3}}{k\mathrm{T}}} + 1} \quad; n_4 = \frac{1}{e^{\frac{\mathrm{E_4}}{k\mathrm{T}}} - 1}$$

we easily get, because

$$\mathrm{K}n_1 n_2 = \mathrm{K}' n_3 n_4$$

$$\text{and } \left(\frac{1}{n_1} - 1\right)\left(\frac{1}{n_2} + 1\right) = \left(\frac{1}{n_3} - 1\right)\left(\frac{1}{n_4} + 1\right)$$

for the probability of a Compton collision considering the fact that n_3 and n_4 are small compared with unity, the expression

$$\mathrm{K}.\,n_1 \; \frac{e^{\frac{h\nu}{k\tau}}}{\left(e^{\frac{h\nu}{k\mathrm{T}}} - 1\right)\left(e^{\frac{h\nu'}{k\mathrm{T}}} - 1\right)}$$

which thus depends upon the frequency of the quantum after recoil. This is the same formula as that given by Pauli,[2]

[1] P. A. M. Dirac, 'Monthly Notice, Vol. 85, p. 830 (1925).

[2] W. Pauli Jr., Zeits für Physik. 18, 272 (1923).

2. *Compton-Scatterring with Bound Electrons.*

Consider a system of unit volume under equilibrium conditions containing N_i atoms in the state i which are capable of being ionised to a further state j. If ϵ_∞ is the energy necessary for ionisation we may think of the ionisation process as commencing with a quantum of energy $\epsilon_\infty + \epsilon_1$ colliding between an atom in the state i, and ending with an atom in the ionised state j, the colliding quantum having dropped in energy content to a new value ϵ_2 and the dislodged electron going off with energy ϵ_8 where

$$\epsilon_1 = \epsilon_2 + \epsilon_8.$$

For the number of quanta having energy between $\epsilon_\infty + \epsilon_1$ and $\epsilon_\infty + \epsilon_1 + d\epsilon_1$ we can write Bose's expression

$$= \frac{A.dE_1 \sqrt{E_1}}{e^{\frac{\epsilon_\infty + \epsilon_1}{kT}} - 1} \quad \text{[where A is the number of cells]}^a$$

The chance that these quanta will make any collision with an atom in the state i will evidently be proportional to the numbers of quanta and atoms, to the cross section of the atom and the velocity c with which the quanta are moving. (It is assumed that the atoms have a speed not very much comparable with that of light.) Hence the number of collisions of the 'first kind' in which the quanta ionise to the atoms i by Compton collision is given by

$$Z_{+i+j} = P_{+i+j} \times N_i \times \frac{A\sqrt{\epsilon_\infty + \epsilon_1}}{e^{\frac{\epsilon_\infty + \epsilon_1}{kT}} - 1} \cdot \frac{1}{c}$$

where the probability factor P_{+i+j} may be thought of as the product of the cross section of atom and the chance that a collision will be successful.

---

^{a} $E_1 = \epsilon_\infty + \epsilon_1$

Let us now consider the 'inverse process' which will lead to the recapture of an electron by an ionised atom in the $-j$ state. Three bodies will evidently be involved in such a recapture : (1) an ionised atom in the state $-j$, (2) an electron with energy

$$\epsilon_3 = \epsilon_1 - \epsilon_2$$

and (3) a quantum with energy ϵ_2 which will aid in the recapture by carrying the excess energy. The electron and the quantum in this process should be moving towards the atom as at the end of the Compton collision.

Since the chance that an ion and an electron are located together in any chosen volume is proportional to the numbers of each present, and the chance that such a pair will be hit by a quantum is proportional to number of quanta of such energy and velocity c with which the quanta are moving.

If the number of atoms in the ionised state $-j$

$$= N_{-j}.$$

Number of electrons in the energy range ϵ_3 and $\epsilon_3 + d\epsilon_3$ is given by the statistics of Fermi and Dirac

$$= \frac{1}{h^3} 2\pi(2m)^{\frac{3}{2}} \, \epsilon^{\frac{1}{2}} \, \frac{d\epsilon_3}{e^{a + \frac{\epsilon^3}{kT}} + 1}$$

Number of Quanta is given by

$$= \frac{A_{\cdot} . d\epsilon_2 \, \sqrt{\epsilon_2}}{(e^{\frac{\epsilon^2}{kT}} - 1)}.$$

Hence the probability of an inverse process is

$$Z_{-j-i} = P_{-j-i} \times N_{-j} \, \frac{1}{h^3} . 2\pi . (2m)^{3/2} . \epsilon_3^{\frac{1}{2}} \frac{d\epsilon_3}{e^{a + \frac{\epsilon_3}{kT}} + 1}$$

$$\times \frac{A_{\cdot} d\epsilon_2}{(e^{\frac{\epsilon_2}{kT}} - 1)} \, \frac{1}{c} \, \sqrt{\epsilon_2}$$

The number of the two must be equal and according to the principle of microscopic reversibility, we get introducing the condition

$$\epsilon_1 = \epsilon_2 + \epsilon_3$$

$$P_{+,+,} . N_i \; \frac{1}{e^{\frac{\epsilon_\infty + \epsilon_1}{kT}} - 1} \cdot \sqrt{\epsilon_\infty + \epsilon_1}$$

$$= P_{-,-,} . N_{-,} \frac{\sqrt{\epsilon_3} . \sqrt{\epsilon_2}}{\left(e^{a + \frac{\epsilon_3}{kT}} + 1\right)\left(e^{\frac{\epsilon_2}{kT}} - 1\right)} \cdot \frac{2\pi(2m)^{3/2}}{h_3}$$

For pair of transitions $-i$ to j and $+j$ to i and also i to $-j$ and j to $-i$ we get similar expressions and so we get finally

$$\frac{P_{,j}}{P_{ji}} = \frac{N}{N_i}, \cdot \frac{\left(e^{\frac{\infty + \epsilon_1}{kT}} - 1\right)\sqrt{\epsilon_2 . \epsilon_3}}{\left(e^{a + \frac{\epsilon_2}{kT}} + 1\right)\left(e^{\frac{\epsilon_2}{kT}} - 1\right)} \frac{2\pi(2m)^{3/2}}{\sqrt{\epsilon_\infty + \epsilon_1} h^3}$$

It can easily be shown that if there is equilibrium (thermal) between the atoms in the i and the j state and the free electrons
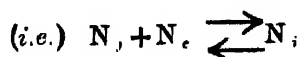
$$(i.e.) \quad N_j + N_e \; \rightleftarrows N_i$$

$$\text{Then } \frac{N_j \times N_e}{N_i} = \frac{(2\pi m kT)^{3/2}}{h^3} \cdot \sigma . \; e^{-\frac{\epsilon_\infty}{kT}}$$

where $\sigma =$ the symmetry factor

    = No. of electrons in the same shell of the i-atoms.

Also in the Fermi-Dirac statistics

where

$$N_i = \frac{(2\pi m k T)^{3/2}}{h^3} \cdot F(a)$$

where $F(a) = \dfrac{2}{\sqrt{\pi}} \displaystyle\int_0^\infty \dfrac{x^{\frac{1}{2}}\,dx}{e^{a+x}+1}$

$$= e^{-a} \quad \text{for a first approximation}$$

Hence we get

$$\frac{N_2}{N_i} = \sigma. \; e^{-\frac{\epsilon_\infty}{kT}} \, F(a)^{-1}$$

Hence our final expression for the ratio of the two probability coefficients is

$$\frac{P_{ij}}{P_{ji}}$$

$$= \frac{2\pi. \, (2m)^{\frac{3}{2}}.\epsilon_3^{\frac{1}{2}}.\epsilon_2^{\frac{1}{2}}}{h^3 \; \sqrt{\epsilon_\infty+\epsilon_1}.\; F(a)} \frac{\left(\dfrac{hv}{e^{kT}-1} \right)}{\left(e^{\frac{hv'}{kT}} - 1 \right)} \cdot \frac{\sigma e^{-\frac{\epsilon_\infty}{kT}}}{\left(e^{a+ \frac{hv-hv'-\epsilon_\infty}{kT}} +1 \right)}$$

where $hv =$ the energy of the initial quanta.

$hv' =$ the energy after scattering

which gives $hv + hv' - \epsilon_\infty =$ as the energy of recoil.
As an approximation we may write

$$\frac{P_{ij}}{P_{ji}} = \frac{2\pi(2m)^{\frac{3}{2}}}{h^3} \; \epsilon_3^{\frac{1}{2}} \cdot \sigma$$

If the energy of recoil is expressed by $\tfrac{1}{2}mv^2$ we get

$$\frac{P_{ij}}{P_{ji}} = \frac{4\pi}{h^3} m^3 v = 3{\cdot}631 \times 10^{17} \times v \times \sigma.$$

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3. *Ionisation by Electronic Impact.*

The problem treated above naturally leads to another, the ionisation by Electron Impact. This problem is treated very elegantly by R. C. Tolman in his Statistical Mechanics. This problem is exactly the same as the one treated in the previous section provided we substitute 'electron' for 'quantum.' In the treatment by Tolman, he uses for the "electron-gas" the Maxwell-Boltzmann statistics. The electron-gas at ordinary temperatures is a degenerate system. So the Fermi-Dirac statistics should be used. The problem can exactly be followed as in the treatment by Tolman, substituting the new-statistics for the old. It is of interest to find the nature of the final expression when we use the new statistics.

For the direct collision we get probability

$$P_{i,j} \quad Ni' \quad \frac{1}{e^{a + \frac{E_1}{RT}} + 1} \cdot E_1^{\frac{1}{2}} \sqrt{\frac{2E_1}{m}} \cdot 2\pi(2m)^{\frac{3}{2}} \, dE_1$$

where E_1 is the initial energy of the electron greater than ϵ_∞

For the collision of the second kind we get

$$P_{j,i} \quad Nj \quad \frac{1}{\left(e^{a + \frac{E_2}{RT}} + 1\right)\left(e^{a + \frac{E_3}{RT}} + 1\right)} \left[2\pi(2m)^{\frac{3}{2}}\right]^2$$

$$\times \sqrt{\frac{2E_2}{m}} \times E_3^{\frac{1}{2}} \, E_2^{\frac{1}{2}} \, dE_2,$$

where $E_2 =$ the energy of the recoil electron.

$E_3 =$ the energy of the initial colliding electron after the collison. So that

$$E_1 = E_2 + E_3 + \epsilon_\infty$$

Hence

$$\frac{P_{ij}}{P_{ji}} = \frac{N_j}{N_i} \frac{e^{\alpha + \frac{E_1}{RT}} + 1}{\left(e^{\alpha + \frac{E_2}{RT}} + 1 \right)\left(e^{\alpha + \frac{E_3}{RT}} + 1 \right)} \cdot 2\pi \cdot (2m)^{\frac{3}{2}}$$

$$\times \frac{E_2 E_3^{\frac{1}{2}}}{E_1}$$

Simplifying for $\dfrac{Nj}{Ni}$ we get

$$\frac{Pij}{Pji} = \frac{\left(e^{\alpha + \frac{E_1}{RT}} + 1 \right) \sigma \cdot 2\pi \cdot (2m)^{\frac{3}{2}} \cdot E_2 \cdot E_3^{\frac{1}{2}}}{F(\alpha) e^{\frac{\epsilon_\infty}{RT}} \left(e^{\alpha + \frac{E_2}{RT}} + 1 \right)\left(e^{\alpha + \frac{E_3}{RT}} + 1 \right) E_1}$$

an expression analogous to that for the Compton and the Reversed Compton collision. *Hence, ' Ionisation by Electronic impact ' is a kind of Compton scattering.*

4.   *An Explanation for the softening of Hard Radiation created in the Interior of a Star.*

"To justify the theories of the source of stellar energy we must satisfy ourselves that the star contains the necessary mechanism for transforming the high-frequency radiation (created in it) into a normal form of energy."[*] This is explained as due to Compton scattering with electrons the wave-length being increased after each collision.

In an atmosphere containing quanta of such high energy it is impossible to conceive of free electrons not having on the average, the energy of the quanta themselves. Because by the ordinary process of Compton scattering the average energy of electrons is increased. This will continue till the average energy of the electrons becomes equal to that of the quanta. So if in one collision a quantum is softened in another it is hardened.

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* A. S. Eddington, 'Internal Constitution of Stars,' p. 316.

If it is then not possible to explain the softening of radiation by the Compton-scattering with free electrons then the only other alternative is that it may perhaps be with bound electrons and the equations arrived at in the previous sections support this conclusion. *If there is thermodynamic equilibrium*, the product of the numbers of electrons, quanta and ionised atoms present in 1 cm^8 (probability of the 'Reversed Compton' scattering) has to be multiplied by a factor of the order of 10^{-27} to make it equal to the product of the numbers of quanta and atoms (probability of the Compton scattering). The former, in our conception, represents the process by which the quanta are hardened, and the latter by which the quanta are softened. In a star therefore where there is no thermodynamical equilibrium it is the direct scattering which is *much more* probable than the ' reversed scattering.' This conclusion is a natural consequence of our conception of the ' Reversed Compton Effect ' with bound electrons. It may be argued that there can be fundamentally no difference between Compton-Scattering with bound and free electrons, for there is a gradual transition from one to the other. But our conception of the ' Reversed Compton Scattering ' with bound electrons, *however weak the binding may be*, is fundamentally different. ' The Reversed Compton-Effect ' with bound electrons is one of triple collision, whereas that with free electrons is an ordinary collision of two bodies. Hence the divergence of the results in the two cases. To conclude, it is perhaps the Compton-scattering with bound electrons that contribute very largely to the softening of the radiation than that with free electrons.

I have great pleasure in expressing my thanks to Mr. S. P. Venkateswaran with whom this problem was discussed a number of times.

Presidency College,   *28th September, 1928.*
      Madras.

Annual Report for 1927.

The Honorary Secretary begs to submit to the Committee of Management of the Indian Association for the Cultivation of Science, the following report on the activities of the Association during the year 1927 :

PART I.

Report on Scientific Investigations.

1. X-Ray Diffraction in Liquids.
2. Molecular Scattering of Light.
3. Artificial Birefringence in Liquids.
4. Other Optical Investigations.
5. Magnetic Researches.
6. Acoustical Investigations.
7. Pleochroic Haloes.
8. A New Synthetic Resin.
9. List of Papers published in 1927.

PART II.

Administrative Report.

10. Our Research Workers.
11. Lecture Arrangements.
12. Laboratory Equipment.
13. Library and Reading Room.
14. Workshop.
15. Financial Statement.
16. Acknowledgments.

PART I.

REPORT ON SCIENTIFIC INVESTIGATIONS.

Following the precedent of earlier reports, it is proposed in the following pages to give in a form as free from technicalities as possible, a general account of the scientific results published during the year 1927, of the work done under the general direction of your Honorary Secretary. Such an account appears desirable, especially in view of the fact that the scientific papers from the Association lie scattered in about a dozen different technical journals. It is hoped that this part of the Annual Report may be of interest to a wide circle of readers.

1. *X-Ray Diffraction in Liquids.*

An important development in our work has been the starting of X-ray research in our laboratories by Mr. C. M. Sogani and subsequently by others. This work is in a sense a natural development from the investigations on light-scattering carried on for several years in our laboratory.

X-rays, as is well-known, form a powerful tool of research in the study of the ultimate constitution of matter. Their value lies in their short wave-length which is of the same order as molecular and atomic dimensions. The theoretical limit of the microscope, using ordinary light, is such that we cannot hope by its help to determine the shape of a body much smaller than a wave-length of light, 0·0005 mm. If an X-ray microscope could be devised, this limit could be reduced by a factor of 10,000 which would take us into the region of atoms and molecules and, in fact, enable us to work on a sub-atomic scale. It is true that such an instrument does not exist, but interference effects are measurable due to X-rays traversing groups of atoms and molecules, and from them we are able to interpret

the structure of the matter giving rise to the diffraction almost as completely as if we were employing an X-ray microscope. The value of the method has already been amply demonstrated in the unravelling of the ultimate regularity of the arrangement of atoms and molecules underlying one of the most marvellous architectures of nature, namely the crystal. We shall presently see that the X-ray method affords us much help in understanding also the ultimate structure of liquids regarding which comparatively little was known until recently. Extensive investigations were undertaken in our laboratory by Mr. Sogani [1] on this subject and valuable results have been obtained.

In the actual experiments the following arrangement of apparatus is employed. A beam of X-rays from the copper target of a metal Shearer X-ray tube is allowed to fall on the liquid after passing through a long narrow aperture in a lead block. The liquid is contained in a brass cell with mica windows, the object of using windows of a crystalline material like mica being to avoid confusion due to the superposition of the diffraction-pattern of a celluloid or glass container which gives a pattern similar to that of a liquid. The beam of X-rays, after traversing the liquid, is received on a photographic plate placed at some distance behind it. The resulting photograph shows in addition to the direct spot a diffraction-pattern or halo, the details of the structure of the halo depending upon the nature of the liquid and being a characteristic of it.

Notwithstanding the fact that the X-ray diffraction-pattern changes from liquid to liquid, there are nevertheless certain features common to all liquids. The essential features are (1) that the intensity of scattering at small angles is usually small, (2) that a considerable part of the scattered energy appears within a certain rather small range of angles,

[1] C. M. Sogani, Ind. J. our Phys., Vol. I, Part IV, p. 357 and Vol. II, Part I, p. 97.

thus forming a marked halo detached from the direction of the primary beam, and (3) that the intensity falls down again at still larger angles. The halo which is always broad or diffuse and is thus clearly distinguished from the multiplicity of sharp rings or spots obtained in the powder or Laue-spot methods from crystals, shows an intensity distribution which differs from liquid to liquid, the halo often possessing two distinct maxima.

Optical Analogies.

An idea of the nature of the X-ray liquid halo may be obtained from the numerous photographs that have been published in our proceedings in the year under report.[1] To understand the simpler type in which there is a single maximum we will consider a few optical analogies and see how far these help us to get a clear conception of the X-ray case.

The first analogy that suggests itself in this connection is that of the coronas which are sometimes seen surrounding the sun or the moon. These coronas are due to diffraction by small drops of water of roughly uniform size distributed sparsely as a cloud in the atmosphere. On account of the want of dense packing of the water-drops, however, the corona bears a closer relation to the case of X-ray scattering by a gas than to the case of scattering by the dense aggregation of molecules in a liquid. The analogy between a corona and the X-ray haloes in liquids is thus unsatisfactory. This is clearly shown by the fact that the scattering at small angles in the coronas is not small but is quite considerable, thus giving rise to the broad disc of light immediately surrounding the sun or the moon. In this case we know that the diffraction-pattern does not arise from the arrangement of the drops, which is entirely chaotic, but is due to the

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[1] C. M. Sogani, *loc. cit.*

individual drops, the effect of a large number of drops being simply to multiply the expectation of intensity at each point of the diffraction-pattern by the number of drops. A laboratory illustration of the corona and therefore also of X-ray scattering by a gas is furnished by viewing a small source of white light through a glass plate, on the surface of which lycopodium has been dusted, or better, by viewing the light through a large wetted glass flask, in which a cloud is formed by expansion. In both the cases, there is a broad disc of light immediately surrounding the source followed by a number of brilliantly coloured rings. The reason why the phenomenon is more clearly resolved and therefore more beautiful in these laboratory experiments is the greater uniformity of size of the diffracting particles.

A more satisfactory optical analogy to X-ray diffraction in liquids is furnished by the case of a breathed-on glass plate, the experiment being more convenient if the plate first receives a deposit from the fumes of ammonium chloride before being breathed on. As an examination under the microscope will at once show, the particles of ammonium chloride which are approximately of uniform size, are fairly densely packed together. We have a two-dimensional analogy to the case of the densely-packed molecules in a liquid. When a small source of light is viewed through the film, we do not observe in this case a disc of light immediately surrounding the source. On the other hand, the halo is separated from the source by a dark space as in the X-ray liquid halo. In this case the halo is not due to the diffraction-pattern of each individual particle but rather to a certain regularity of distribution which the particles possess.

This analogy to the liquid-halo would be perfectly satisfactory except for the reason that it is only two-dimensional, whereas the arrangement of molecules in a liquid is obviously three-dimensional. Perhaps the closest analogy that we know of is furnished by the case of homogeneous chromatic

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emulsions studied by Mr. Sogani[1] in our laboratory and an account of which was given in the report of the preceding year. These emulsions consist of spherical droplets which are more or less of uniform size and are obtained by the sedimentation of the usual non-homogeneous emulsions. As would be seen from the photographs, the particles of the emulsion are more or less closely packed together and form a sort of three dimensional grating which is, however, not quite regular, partly on account of the want of perfect uniformity of size of the particles and partly also on account of certain fluctuations in the distance between neighbouring particles due to the emulsion not being a perfectly closepacked one. In a recent paper by Mr. Sogani,[2] the close analogies between the X-ray diffraction in liquids with spherical molecules, in which case the halo has a simple structure, and the optical haloes we are considering have been pointed out in detail.

The main difference between the X-ray liquid halo and the analogous optical phenomena discussed above lies in the general absence of higher orders in the X-ray case. Only in a few cases, such as for example, carbon tetra-chloride, liquid argon and mercury, have some outer maxima been observed which appear to be of the nature of higher order effects. Even in these cases, the spacings for the various maxima do not have the usual multiple relation. It might be mentioned here that the double haloes obtained in the case of liquids like mesitylene, quinoline, ortho and metanitrotoluenes, acetic acid, etc., are not due to this cause. This is apparent from their intensity relationships, and the two maxima in these cases are first-order effects and have no counterpart whatever in the optical phenomena discussed above. Their significance with regard to the elucidation of the molecular constitution of these liquids will be discussed later.

[1] O. M. Sogani, Phil., Mag. Vol. I, p. 321 (1926).
[2] Ind. Jour. Phys., Vol. II, Part III, p. 877.

Origin of the liquid-halo.

From the various optical analogies discussed above, it would be clear that the X-ray liquid-halo must be due to the co-operation of the various diffracting centres, whatever these might be, in the liquid and not due to a single diffracting centre. A discussion of the actual angular size of the halo further leads one to the view that these diffracting centres are probably no other than the molecules themselves.

It would perhaps be worth while here to consider the general case of the diffraction of radiation by a discontinuous medium consisting of discrete particles, and see how the intensity-distribution in the scattered beam is related to the structure of the medium. The discussion will obviously apply either to the optical cases in which the diffracting particles are relatively big and are of the order of the wave-length of visible light, or to the X-ray case in which we are actually dealing with the atoms and molecules themselves. We are, however, concerned at present only with the latter case.

Consider the medium to be divided up by an infinite number of parallel planes perpendicular to the direction bisecting the angle between the incident ray and the scattered ray. For purposes of interference, it is obvious that the mode of distribution of the particles in these planes is of no importance whatsoever, because the secondary waves from the various points of such a plane would all be in the same phase. Consequently we have only to consider the distribution in a direction perpendicular to these planes. Of these infinite planes, let us for the moment fix our attention on a series separated from each other by such equal intervals that the secondary waves starting from successive planes have a path difference which is equal to the X-ray wave-length. The scattered waves from these planes will therefore reinforce each other in the direction of observation, while those arising from intermediate

planes will oppose their effect. If the distribution of matter within the medium, has a real periodicity with a wave-length equal to the distance between the successive planes, we shall have a strong uncompensated scattering due to the whole medium in the particular direction which we have been considering. Conversely, if there is a maximum of scattering in a particular direction of observation, that would unmistakably point to a real periodicity in the distribution of matter in the medium of an appropriate and calculable wave-length.

The above mode of analysis is due to the Braggs and was advanced by them in connection with the interpretation of the phenomenon of X-ray diffraction by crystals. The method has, however, a much more general application and would apply equally well to the case of liquid-diffraction.

As mentioned before, the simple type of X-ray liquid pattern shows a single more or less broad maximum with a falling-off in intensity on either side. This at once suggests that in the distribution of matter in such liquids, there is a single predominant periodicity which is connected by the usual Bragg formula with the angle of maximum scattered intensity and the X-ray wave-length.

We are now in a position to see that this periodicity is due to a regularity in the arrangement of the molecules themselves, for it is found to be of the same order as the mean distance between neighbouring molecules in the liquid. The latter can easily be calculated if we know the mass of a molecule, the density of the liquid, and assume the molecules to be arranged either chaotically or else in some particular way approximating to a regular geometric ordering. The observed facts in regard to the X-ray liquid-haloes show clearly that we are actually dealing with a certain approximately periodic distribution of the molecules within the liquid. That the periodicity is not exact is shown by the diffuse character of the halo, and this may reasonably be ascribed to the thermal agitation of the molecules in the liquid, and to their

non-spherical shape. This view was adopted in a paper publish-
ed in 1923 by your Honorary Secretary along with Dr. K. R.
Ramanathan[1] under the title "The Diffraction of X-rays in
liquids, liquid mixtures, solutions, fluid crystals and amor-
phous solids," the reason for including the fluid-crystals and
the amorphous solids being that these also give X-ray haloes
essentially similar to those of an isotropic liquid. An attempt
was made in that paper to find theoretically the distribution
of intensity at different scattering-angles in the diffraction
pattern. It is obvious that though we have a predominant
periodicity equal to the average distance between neighbour-
ing molecules, other periodicities are also present as shown by
the considerable width of the halo, and by the fact that there
is appreciable scattering both at small as well as large angles
outside the principal halo. Obviously, each scattering angle
can be referred to a periodicity of corresponding wave-length,
the relative probability of which is proportional to the intensity
of scattering at this particular angle. The problem then is to
find values for the relative probabilities of different periodici-
ties from theoretical considerations and see how far theory
helps us to explain the actual observed facts.

The well-known thermodynamic principle connecting
entropy and probability due to Boltzmann enables us to cal-
culate the magnitude of the spontaneous fluctuations in den-
sity within a liquid. It is found that these fluctuations
depend on the compressibility of the liquid and its tempera-
ture, and that with the aid of the Boltzmann principle, the
optical opalescence of liquids may be successfully explained.
The fluctuations of density naturally involve corresponding
variations in the periodic distribution of matter within the
liquid which give rise to the X-ray haloes. Hence, it becomes
possible, at least in relatively simple cases, to express the

[1] C. V. Raman and K. R. Ramanathan, Proc. Ind. Assn. Cult. Sc., Vol. VIII, Part II,
p. 127 (1923).

probability of different periodic distributions of the molecules in terms of the absolute temperature, the compressibility and density of the liquid. On these lines, Raman and Ramanathan obtained a theoretical expression which when plotted with the data for benzene gave a curve in fair agreement with the experimental results for X-ray diffraction in the liquid obtained by Hewlett. The theory further predicts that the sharpness of the halo should be influenced by the compressibility of the liquid and its temperature. Other things being the same, the halo should become more diffuse with an increase in the value of the compressibility and with rise of temperature. Both these predictions have now been tested in our laboratory.

Mention may here be made of the special case of X-ray scattering at small angles, as this forms a connecting link between light scattering and X-ray scattering, and admits of a simpler treatment. For, the distance between the successive planes separated by a path-difference of one wave-length would then comprise several molecules. In order, therefore, to calculate the scattering at sufficiently small angles, we can employ the method of Smoluchowski and Einstein in which the discrete molecular structure is ignored, and the liquid is treated as a structureless continuum subject to local changes of density determined by thermodynamical considerations. This method yields the same results as those given by a more explicitly molecular treatment in the optical region where the wave-length is large in comparison with molecular dimensions, and would also apply to the case of X-ray scattering at very small angles. As a consequence it can be shown that the scattering in this special case will be directly proportional to the compressibility and the absolute temperature as in the optical case, no matter whether the diffracting medium is a liquid, an amorphous solid or a crystal. It is understood that we are here assuming the molecules to be of the simplest type possible so that their variations of orientation may be ignored.

Molecular form and symmetry.

We have so far been mainly concerning ourselves with the general features of the liquid-halo and practically ignoring the remarkable variety in its structure. We know however that great differences between one liquid and another are shown by every one of their properties. May we not then ask, "Is the difference between one liquid and another also shown by the X-ray halo?" The answer is emphatically in the affirmative, as would be shown by a glance at the various photographs in Mr. Sogani's papers. Indeed it would be no exaggeration to say that a liquid can be recognised by its characteristic X-ray halo nearly as well as by any of its other physical properties. The statement particularly applies to the case of the benzene derivatives in which the halo undergoes a remarkable progressive change in structure as we pass to more and more complex derivatives and the important part played by the geometrical form and symmetry of the molecule is brought out in a striking manner.

Starting with the simple sharp halo for benzene and cyclohexane, we have in some cases haloes nearly three times as broad (nitro-benzene) and in several cases (mesitylene, ortho and meta nitro-toluenes, etc.) the halo develops a further interesting feature and is broken up, as it were, into two more or less equally bright maxima with a comparatively dark space between. Not only does the structure of the principal halo alter when we pass from one benzene derivative to another with a different molecular formula, but even the minor differences between the spatial arrangement of atoms or groups constituting different isomeric molecules are also found to be clearly reflected in the structure of their haloes (ortho, meta and para xylenes and nitro-toluenes). A further examination of the aromatic compounds undertaken by Mr. P. Krishnamurti[1] with a view to examine if any general relationship exists between

[1] Ind. Jour. Phys., Vol. II, Part III, p. 855.

the positions of the substituent groups in the benzene ring
and their X-ray haloes show that the regularities observed in
the case of the three xylenes and nitro-toluenes by Mr. Sogani
are probably general features associated with the ortho, meta
and para modes of substitution. The differences become
striking when the substitution groups are fairly big in which
case the ortho and meta give two well-defined maxima, where-
as the para gives only a single very diffuse maximum.

The longchain aliphatic liquids studied also show
differences in their haloes which are, however, not quite so
striking. In some cases (*e.g.*, acetic acid and glycerine), we
get in addition to a strong outer halo, a second inner halo
which however is comparatively feeble. One important
feature of the haloes in the case of the aliphatic liquids must
be pointed out, namely, that there is a considerable amount of
scattering at small angles even in cases where no distinct
inner maximum is observed. This naturally suggests the
presence of an unresolved inner maximum in these cases.
Further the principal halo also shows different degrees of
sharpness for different liquids as might be seen by a compari-
son of the series pentane, hexane, heptane and octane.

Radius of the halo.

A measurement of the radius of the halo in the various
cases is no less instructive than a study of its structure. We
have seen already that the principal periodicity in the spacing
of the molecules calculated from the size of the halo and the
Bragg formula is of the same order of magnitude as the mean
molecular distance calculated on the assumption of a cubic
ordering of the molecules. A detailed study however shows
that this is by no means exactly true in every case. It is
very nearly exact in the case of monatomic elements (mer-
cury), liquids with small molecules (methyl alcohol, formic
acid, benzene) and liquids with highly symmetric molecules

carbon tetrachloride). But, in the case of the series of long-chain compounds, the molecular spacing instead of increasing with increasing molecular weight, actually attains a constant value when the chain contains more than 4 or 5 links. (We are here referring to the spacing given by the principal halo.) In the case of the benzene derivatives, which give two haloes, we have evidently to reckon with two different spacings, one of which is greater and the other less than the average distance between the molecules.

We will now proceed to see what information these results furnish with regard to the elucidation of the nature of the liquid state.

Nature of the liquid state.

Before discussing the direct evidence furnished by our X-ray investigations on this fundamental point, we may refer briefly to the information which our previous investigations on light-scattering had afforded. A study of the variations in the intensity of the transversely scattered light as we pass from the case of a rarefied gas to that of a liquid far below its critical temperature is very instructive. It is observed that the intensity increases proportionately with the density of the gas so long as it obeys Boyle's law. This result indicates that the molecules in this case are distributed at random in space. In denser media and especially in liquids this simple relation fails, and we infer that the molecules can no longer be considered to be arranged at random, and that their positions in space must possess a certain degree of regularity, the regularity obviously increasing as the density is increased. The existence of such regularities compels us to take into account the co-operation of the scattered waves sent by the individual molecules in the liquid. It is this same regularity which is brought home to us by the X-ray haloes in liquids. That the regularity is of a lower type than that obtained in

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crystals and is even generally weaker than that obtained in the optical analogue of the chromatic emulsions, is shown by the absence of rings of higher orders except in the cases of highly symmetric molecules such as carbon tetrachloride.

Instructive as the simplest type of X-ray halo is, much further information as regards the nature of the liquid state is furnished by the case in which the halo either shows two maxima or shows a single maximum of abnormal size as in the case of the long-chain compounds. As mentioned before, the existence of an appreciable amount of scattering inside the halo in the latter case may be interpreted as due to a feebler unresolved inner maximum. The problem now is to understand how two maxima arise in the liquid halo. It may be repeated again that both these maxima are first-order effects and find no counterpart in the optical analogies. This dissimilarity between the optical and the X-ray cases may indeed give us a clue to the solution of the problem. In the optical analogies, for example, those of the breathed-on films and the chromatic emulsions, the diffracting particles are all spherical, though not exactly of the same size. On the other hand, the molecules of a liquid, we know, possess all varieties of shapes, some being nearly spherical, others elongated and still others being disc—like structures. Now as the anomalous cases in the X-ray halo occur only in liquids whose molecules have a distinctly asymmetric shape, one would naturally be led to associate the two maxima with the asymmetry of the molecule. The exact view put forward [1] is that in the case of liquids having molecules whose shape departs considerably from spherical symmetry, neighbouring molecules of a liquid are not orientated at random relatively to each other, for otherwise we would not have two different periodicities, but only a single periodicity corresponding to an

[1] C. M. Sogani, *loc. cit.*, paper II, p. 108.
See also Raman and Ramanathan, *loc. cit.*, p. 154.

averaging of the various orientations. On the other hand it is suggested that in a dense aggregation like a liquid, these asymmetrical molecules exercise an orientative influence on one another so as to bring about a rough parallelism between the neighbouring molecules. In such a case, it is obvious that an analysis of the structure of the liquid will give us two periodicities corresponding to the two principal dimensions of the molecule. For example in the case of a liquid with elongated molecules possessing such a correlation of orientation, one of the periodicities will correspond to the cross-section and the other to the length of the molecule. The constant value of the size of the halo for the higher members is readily understood if the principal periodicity be identified with the cross-section of the molecule. Further in the case of flat molecules, we shall also have two periodicities, one corresponding to the thickness of the molecule and the other to the diameter of the flat surface.

The above view of the nature of the liquid state is found to be in good agreement with the facts of X-ray liquid-diffraction both for the aliphatic as well as aromatic liquids. For fuller details reference may be made to the original papers.

It may be added that the orientative forces contemplated here need not extend over regions very large compared with molecular dimensions. Moreover it is obvious that they must be restricted to regions small compared with the wave-length of visible light, for otherwise the liquid would no longer be isotropic but would exhibit local birefringence detectable under the polarisation microscope. As to how far the orientative influence would actually extend must depend upon the particular liquid in question.

A question might naturally arise here as regards the nature of these orientative forces in a liquid. Presumably these may be of the same type as those that are operative in a crystal. Only they would be comparatively much weaker on account of the fact that in the rivalry between the attractive

forces and the molecular movements tending to overcome them, the latter have now gained the upper hand.

It might be stated that there is nothing strange about the views indicated above, for, a thoughtful consideration of the simplest property of a liquid, for example density, is sufficient to force them on our attention. The fact that the density of a liquid does not differ much from that of the corresponding crystal with its perfectly orientated assemblage of molecules, is sufficient to convince one that in the case of highly asymmetrical molecules, melting cannot bring about any great change in the orientation of neighbouring molecules, for in that case the density would be considerably reduced on melting, which is however not the case. The wonder rather is that we did not come to think of the matter so clearly before, and the reason is obvious. It lies in the fact that no method at our disposal is able to take us so deep into its structure as the probing by means of X-rays where we directly deal with the separate effects of individual molecules and are enabled to see them actually, as it were.

It may be added that a somewhat similar view-point has also been adopted by Stewart and Morrow[1] in connection with their study of X-ray diffraction in liquid normal primary alcohols. Very interesting work in this field has also been done by J. R. Katz at Amsterdam.

Influence of Compressibility and Temperature.

The theory put forward by your Honorary Secretary in 1923 predicted two effects, namely, the influence of compressibility and of temperature on the liquid halo. The first effect has been verified in a general way by Mr. Sogani and it has been found that as predicted, the diffuseness of the halo is determined by the value of the compressibility especially in the case of the liquids which give a single maximum as for

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[1] G. W. Stewart and R. M. Morrow, Phys. Rev., Vol. 30, p. 232 (1927).

example the aliphatic hydro-carbons pentane, hexane, heptane and octane. In the case of the more complex haloes (benzene derivatives), the influence of molecular form and structure is however much too predominant and the influence of compressibility cannot be so satisfactorily traced.

The investigation of the effect of temperature was undertaken by Dr. N. K. Sethi of the Benares Hindu University who was with us during the summer. The same subject was also taken up by Mr. S. S. Ramasubrahmaniam. Valuable results have already been obtained, which support the predictions of the theory. A number of liquids have been examined at various temperatures and in addition a few amorphous substances have also been studied on either side of the softening temperature. As predicted, the liquid halo is found to degenerate, becoming more and more diffuse as the temperature is raised. Besides, the halo is found to contract remarkably in size also. The progressive degeneration of the halo with temperature shows us in a striking manner how, as the temperature is raised, the molecular movements get the upper hand of the attractive forces and the ordering of the molecules tends further and further towards the chaotic state. Thus X-rays not only enable us to perceive the order as well as want of order underlying the molecular arrangement in a liquid, but also help us in watching the rapidity with which this order gradually gives place to chaos, the process being of course completed only when the liquid is transformed into a very attenuated vapour or gas.

2. *Molecular Scattering of Light.*

The subject of light-scattering which has been engaging our attention during the last six or seven years still continues to be one of the most fruitful lines of research in our laboratory. In fact the subject was approached from various aspects during the year under report and it may fairly be

claimed that, viewed from the classical side of the subject, many of the outstanding problems both on the theoretical and on the experimental sides have been successfully attacked.

The molecular theory on the subject which was developed by Dr. K. R. Ramanathan, has been discussed in detail in our previous reports. It explains in a general way all the essential features of the phenomenon, and has been the guiding theory in all our previous investigations. But a critical discussion by Mr. K. S. Krishnan of the extensive measurements made available since the publication of Ramanathan's theory, showed that a modification was necessary in two directions. In the first place the intensity of the scattered light actually observed is slightly but definitely smaller than the value given by Ramanathan's formula. The second point is a little more complicated. It has been mentioned in our previous reports that one characteristic feature in scattering is that even when transversely observed it is not completely polarised. This fact receives a natural explanation in the theories of Raman and Ramanathan when the optically asymmetrical nature of the molecules of the scattering medium is taken into account. In that case one would expect the degree of asymmetry required to explain the imperfection of polarisation mentioned above, to be characteristic of the particular type of molecule and independent of its state of aggregation. But as a matter of fact, observations suggest that the asymmetry is apparently very much less marked in the liquid state than in the vapour state.

The first modification of Ramanathan's theory came from Ramanathan himself, and offers a convincing explanation of the observed intensities. In order to make the significance of this modification clear it is necessary to recall some of the fundamental postulates in his previous theory. Under the influence of the incident light waves the individual molecules in the medium behave like oscillating electric doublets— the electrical analogues of magnetic particles—which as a

consequence radiate out energy. The phase of the radiation starting from any given molecule is determined by the phase of the incident radiation exciting it. Now if the molecules were arranged in a perfectly regular order so that their number per unit volume at different parts of the medium would be exactly the same, then it is obvious that the effect of the molecules in any small volume element would be completely destroyed by interference by that of the molecules in another equal volume-element suitably chosen. Hence there would be no lateral scattering, the whole of the incident energy then passing straight through the medium without any loss on account of scattering.

But as a matter of fact such a regularity in arrangement contemplated in the above discussion does not exist even in crystals, because the molecules are free to execute thermal oscillations about certain mean positions. When we come to any actual liquid, the movements due to thermal agitation are so conspicuous that considerable fluctuations of density must occur and hence a conspicuous lateral scattering.

Theory of Scattering.

When we try to evaluate the intensity of the scattering on this basis the question immediately arises as to what is the actual magnitude of the force which induces the doublets in the molecules. Is it only the electric force of the incident light wave or do the doublets induced in the surrounding molecules also contribute to it ? The significance of the question can be made clear by going back to the magnetic analogy. Suppose we have a small needle suspended at some distance from the pole of a large bar magnet. The needle as is well-known, becomes temporarily a magnet (or an induced magnet in the phraseology we have been using) and tends to point towards the pole. If we take several similar small needles each one of them by itself will behave in the same manner.

But when they are all suspended close to one another, but still sufficiently clear of one another's movements, it is evident that they will begin to influence one another's setting, that is to say, when considering the setting of any particular needle we have to consider not only the influence of the bar magnet but also of the temporarily magnetised needles surrounding it. The problem is exactly the same in the electrical problem we are considering. We have not only to take into account the electric force in the incident light-wave, but also the force due to the doublets induced in the surrounding molecules. The question of actual evaluation of the latter has been considered in detail by Lorentz and he comes to the conclusion that in dense media, this force, which he calls the polarisation field, is very considerable.

From the foregoing discussion it is natural to suppose that the influence of the surrounding molecules must depend, other things being equal, on their number per unit volume. If, as we have pointed out, their number fluctuates owing to thermal agitations, will the polarisation field also fluctuate? The answer at first sight seems to be that they certainly should. In any case that was the answer on which Ramanathan's earlier theory was based. But in view of the need for a modification of his earlier theory he has reconsidered the question and comes to a different conclusion. He emphasises that we have to distinguish between two kinds of fluctuations of density of the medium, one, a uniform change of density throughout the medium, and another, the *local* fluctuations of density which do not however affect the mean density of the medium as a whole. It is only in the former case that the polarisation field due to the surrounding molecules would vary correspondingly, whereas in the latter type of fluctuation, which is in fact the one responsible for scattering, where the mean density of the medium as a whole does not vary, the polarisation field must be considered to be unaffected.

On the basis of this conclusion Ramanathan has modified his previous formulae and it is found that the values of the intensity predicted by this modified theory agree satisfactorily with the actual observations.

But the theory leaves practically unsolved the second difficulty mentioned in the earlier part of this section regarding the apparent change in the optical asymmetry of the molecule as it passes from the state of vapour to that of liquid. The clue to the explanation of this discrepancy came however from the X-ray investigations carried out in our laboratory, and we will reserve a detailed consideration to a later section of the report. In fact the difficulty is not peculiar to the theory of light-scattering. It appears in more or less the same form in the theories of other optical and electrical properties of liquids, and they will be considered together in that place. For the present we will content ourselves by merely drawing attention to it as a typical example of how investigations in different branches react on one another. The development of the theory of X-ray scattering in liquids owed much to light-scattering, and now comes the turn of the former to throw light on some unsolved problems in optical scattering.

Scattering in Protein Solutions.

Early in 1923, the present writer with Dr. Ramanathan put forward a theory of light-scattering in binary liquid mixtures, and showed that in addition to the scattering arising from the thermal fluctuations of density, and the varying orientations of the asymmetric molecules as in a single medium, the scattering due to the fluctuations in concentration of the mixture has also to be taken into account. The theory has now been extended by the present writer to the case of colloidal solutions [1] which enables their light-scattering power

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[1] C. V. Raman, Ind. Jour. Physics, Vol. II, Part 1, p. 1 (1927).

to be evaluated in terms of the variations of the osmotic pressure and the dielectric constant of the medium with the concentration of the dispersed material. The theory offers a ready explanation of the well-known opalescence exhibited by gelatine solutions when their hydrogen ion concentration approaches the value corresponding to the isoelectric point.

Scattering in Amorphous Solids.

It has been mentioned in the previous section that the scattering by liquid mixtures can be ascribed to fluctuations of density as well as of concentration and to the varying orientations of the asymmetric molecules in the medium. When the mixture is cooled sufficiently low that it congeals to an amorphous solid, we should expect in the first place the compressibility to become very small and consequently the fluctuations of density to fall down considerably. But the fluctuations of composition will tend to increase rather than diminish, while the effect due to molecular orientations would continue almost unaffected in the solid. Thus we may anticipate that amorphous solids such as optical glasses, consisting as they usually do of a mixture of different molecules, more or less asymmetric optically, would exhibit an internal scattering or opalescence of an order of magnitude not greatly inferior to that ordinarily observed in liquids or liquid-mixtures.

These anticipations are fully justified by some observations on Jena glasses made by the present writer.[1] That the opalescence is a genuine molecular scattering of the kind contemplated in the previous paragraph is clear from the fact that its intensity is definitely correlated with the refractive index and with the chemical constitution of the specimen and when transversely observed it is found to exhibit strong polarisation.

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[1]   C. V. Raman, Jour. Opt. Soc. Amer., 15, 185, (1927).

Experimental Studies.

Very extensive experimental studies have also been made on the subject. The extremely careful and painstaking investigations of Mr. I. Ramakrishna Rao[1] on no less than 73 gases and vapours deserve special mention. The numerical values available for the scattering constants of gases and vapours were very meagre and discordant, the values sometimes varying over a large range. Mr. Rao critically studied the errors inherent to the different experimental methods and finally adopted the one which had been previously used by Cabannes, as automatically eliminating to a large extent the disturbing effects of the imperfect background. Also it had been generally supposed that for really accurate measurement the incident beam has to be parallel, and when from considerations of experimental convenience we use a convergent beam, we must necessarily apply a correction for the deviation from parallelism. By actually experimenting with various known apertures Rao comes to the surprising conclusion that the size of the aperture is of no practical importance and gives in fact convincing theoretical explanation of this result.

In the case of liquids Mr. A. N. Banerjee[2] has studied a large number of aromatic compounds, which are of special interest in view of the remarkable optical asymmetry of some of these molecules, and Mr. Ramachandra Rao[3] has investigated some typical liquids over a wide range of temperature up to their critical points. Their results entirely support Ramanathan's modified theory.

The study has been extended by Mr. Venkateswaran[4] to the case of aqueous solutions of both inorganic and organic

[1] Ramakrishna Rao, Ind. Jour. Phys., Vol. II, Part 1, p. 61 (1927).

[2] A. N. Banerjee, Ind. Jour. Phys., Vol. II, Part 1, p. 51 (1927).

[3] S. Ramachandra Rao, Ind. Jour. Phys., Vol. II, Part 1, p. 7 (1927).

[4] S. Venkateswaran, Ind. Jour. Phys. Vol. I, Part IV, p. 393 (1927).

acids. We will mention here only two of the interesting results obtained by him. He finds in the first place that while the solutions of the fatty acids behave like binary mixtures, exhibiting an appreciable concentration scattering, the solutions of mineral acids behave like single substances. Secondly, his observations suggest that the nitric acid molecule has a much more striking optical asymmetry than hydrochloric or sulphuric acid, a result in conformity with Bragg's observations on crystalline nitrates and sulphates.

3.   *Artificial Birefringence in Liquids.*

It is well-known that under the influence of a strong field of force whether electric or magnetic or mechanical, a liquid exhibits a feeble double-refraction. It is usual to describe this kind of double-refraction impressed by an external field as "artificial" in contradistinction to the natural birefringence shown by crystalline substances in the unstrained state. During the year under report the subject has been studied in its theoretical aspects by Mr. Krishnan and the writer, especially in relation to light-scattering with which it is closely connected. The explanation of the general features of the phenomenon is very simple. Our investigations on light-scattering have made familiar to us the fact that the molecules of a medium are in general optically asymmetric. Let us now postulate a general tendency for the molecules under the influence of the impressed fields of force to turn round and take up definite orientations with respect to the field. This tendency will be considerably hampered by the thermal agitations of the molecules. However when equilibrium is attained (of course statistical) there will be a small preponderance of molecules having the above orientation over those pointing in other directions. The individual molecules being themselves optically asymmetric, a natural consequence of any such tendency for them to take up

favoured orientations will obviously be to render the medium as a whole optically asymmetric, *i.e.*, the medium exhibits birefringence in the same manner as a uniaxial crystal.

Electric Double Refraction.

We now proceed to consider the nature of the orientative couple exerted by the external field on the molecules. Let us first take the electrical case. The couple arises in general in virtue of the differences in the induced electrification of the molecule in different directions ; because we have reason to believe that just as a molecule exhibits asymmetry in respect of its optical properties, so it does also regarding its electrical properties. In addition to this the molecule may also show a permanent electrical polarity, having a small positive charge at one end and a large negative charge at the other end. In this case the orientative couple is usually very much greater.

Theoretical considerations show that the former kind of electric asymmetry (*i.e.*, induced asymmetry) is very closely connected with the optical asymmetry with which we are familiar in light-scattering. If we make use of this result, several points in the theory of electric double-refraction which had not been clearly understood till now receive a natural explanation. For example, if there is no permanent polarity in the molecules, the double refraction will always be positive (we borrow here the phraseology of optics of uniaxial crystals), whereas if it has also a polarity, the double refraction may be positive or negative according to the direction of the electrical dipole. The idea can in fact be used in certain cases to calculate the value of the dipole, or when it is already known from other methods to fix its direction in the molecule. For a detailed discussion of these and other points in the subject the interested reader may be referred

to two papers by Mr. Krishnan[1] and the present writer in the Philosophical Magazine.

Magnetic Double Refraction.

Coming now to the magnetic case, here also we have in the first place the orientative couple due to the differences in the induced magnetisation of the molecules in different directions. For example a flat molecule like benzene is found to exhibit a remarkable asymmetry, the power of magnetisation of the molecule perpendicular to the plane of the ring being numerically about twice as large as for directions in the plane.[2] The aliphatic carbon compounds, on the other hand, are relatively more or less symmetrical. But recently the present writer has constructed a large electromagnet, capable of giving a high field over a length of about 30 cms. With the help of this magnet it is found that every substance, including aliphatic hydrocarbons, water, alcohols, etc., shows a feeble but quite definite double-refraction.[3]

The physical reality of the magnetically asymmetric nature of molecules is forcibly brought out by investigations on magne-crystalline action, so widely studied by Faraday, Tyndall and others. On the basis of these ideas, one is enabled to calculate the differences in the susceptibilities of crystals as measured in different directions from purely optical data.[4] Attempts have also been made with fair success to calculate the magnetic asymmetry of the benzene molecule directly from its structure.[5]

[1] C. V. Raman and K. S. Krishnan, Phil. Mag., Vol. 3, pp. 713 and 724 (1921).

[2] C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. A., Vol. 113, p. 511 (1927).

[3] C. V. Raman and I. Ramakrishna Rao, Nature, Vol. 119, p. 528 (1927).

[4] C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. A., Vol. 115, p. 549 (1927).

[5] C. V. Raman and K. S. Krishnan, Comptes, Rendus, Vol. 184, p. 449 (1927).

Are Magnetic Molecules orientated in a Magnetic Field ?

It has already been pointed out that where the molecule has an electric dipole, the orientative couple exerted by the incident electric field on the molecules is mostly the couple acting on the dipole, the couple arising from the induced moments being very much feebler in comparison. Should we not expect a similar result in the magnetic case, *i.e.*, if the molecules are already magnetic should they not orient much more strongly in a magnetic field than when their magnetisation is only induced ? The well-known theory of paramagnetism developed by Langevin essentially postulates such an orientation of the molecules. But some recent experiments, made in our laboratory by Mr. K. S. Krishnan [1] do not give any evidence of such an orientation, and his results seem to suggest that paramagnetism is not a molecular property at least in the sense in which we usually understand it.

Asymmetry of the Polarisation Field.

In connection with the discussion of the asymmetry of the molecule which causes its orientation in an external field we have considered two types, one due to the induced moments and the other to the permanent moments if any in the molecule. But the asymmetry may also arise in an entirely different manner. It was mentioned in an earlier section of this report that when a medium is traversed by light-waves, the calculation of the force acting on any given molecule in the medium must take into account the polarisation field due to the doublets induced in the surrounding molecules. The actual calculation naturally requires a knowledge of the distribution of the molecules surrounding the one under consideration. Lorentz in his treatment of the subject, which now

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[1] K. S. Krishnan, Ind. Jour. Phys., Vol. 1, p. 245 (1927).

forms the basis of many of the optical and electrical theories, assumed the distribution to be spherically symmetrical. But a moment's consideration will easily convince us that this step is no more than a first approximation. When we are dealing with long molecules like hexane or octane (to take extreme examples) it is obvious that their geometric form will necessarily conduce to an asymmetric distribution of the surrounding molecules, especially when they are densely packed as in a liquid at ordinary temperatures. The X-ray investigations described in detail elsewhere in this report support this view, since the spacing given by the prominent diffraction haloes correspond to the cross-sections of these molecules rather than to their mean size. This experimental evidence would seem to compel us to recognize the actual asymmetric nature of the distribution of the molecules surrounding any given one, and the consequent asymmetry of the polarisation field acting on the latter. The theories of refraction, of dielectric polarisation, of electric and magnetic birefringence and of light-scattering will naturally all require modification in the light of the above conclusion, and in a series of papers published by the present writer with Mr. Krishnan,[1] its implications are fully discussed. The modifications proposed have helped us in clearing a number of discrepancies known to be present, in the experimental verification of the existing theories. Before concluding this section we will only point out that it also explains in a quantitative manner the apparent change (mentioned in an earlier section) in the optical asymmetry of a molecule as it passes from the vapour to the liquid and thus offers a solution of the one outstanding difficulty in Ramanathan's theory.[2]

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[1] C. V. Raman and K. S. Krishnan, Proc. Roy. Soc. A., Vol. 117, pp. 1 and 589 (1927-28).

[2] C. V. Raman and K. S. Krishnan, Phil. Mag., Vol. 5, p. 498 (1928).

Mechanical Birefringence in Liquids.

Finally we take up the case of birefringence of liquids under mechanical strain. Maxwell discovered several years ago that a liquid under flow develops a temporary double-refraction whose principal axes are inclined at 45° to the direction of flow. The subject has recently been brought to prominence by the extensive measurements of the effect made by Vörlander and Walter on over a hundred and forty pure liquids.

It is easily seen that the stresses in a flowing liquid can be resolved into a set of tensions and pressures acting perpendicularly to each other and at 45° to the plane of sliding. If therefore we can discover some mechanism by which the molecules tend to orient themselves either in the direction of tensions or along the direction of pressures, we have then by analogy with the electric and magnetic cases a ready explanation of the phenomenon. Such a mechanism is supplied by the elongated geometrical shape of the molecules. Because, if we regard the liquid as a densely packed assemblage of molecules, a tendency for the molecules to orient so as to have their long dimensions along the axis of tension and their broad sides along the axis of pressures, will evidently result in the medium as a whole expanding along the direction of tensions and contracting along that of the pressures, and would thus allow the system of stresses to do work.[1] In view of the optical asymmetry of the molecules, the birefringence then follows as a necessary consequence just as in the case of electric birefringence, to which in fact, when the theory is mathematically worked out, it shows a very close formal analogy. The final formulae are fully supported by the experimental results of Vörlander and Walter.

[1] C. V. Raman and K. S. Krishnan, Nature, Vol. 120, p. 726 (1927).

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4. *Other Optical Investigations.*

Colours of Diffraction.

Many years ago the French physicist Gouy discovered that when a metallic screen with a sharp edge is held in the path of a pencil of white light, the light which bends round the edge is strongly polarised and coloured, the colour and the polarisation depending to a large extent on the material of the screen and on the rounding of its edge in the course of polishing. The well-known rigorous theory of diffraction by a straight edge developed by Sommerfeld pertains to the case of an ideally reflecting screen and it is not therefore surprising that it does not explain many of the observations of Gouy.

A simple theory of at least the essential features of the phenomenon is forthcoming when the imperfect conductivity of the actual screen used is taken into account. So far as the illuminated face of the diffracting screen is concerned, we have only to substitute in place of the reflexion co-efficient unity in Sommerfeld's expressions, the actual metallic reflexion co-efficient (complex owing to change of phase also occurring). As a matter of fact, this modification is also found to give the disturbance not only on the illuminated side but also throughout the medium much more accurately than Sommerfeld's formulae.[1]

On somewhat similar lines, the colour and polarisation effects exhibited by the light diffracted by the edges of thin transparent laminae (*e.g.*, the striae in mica) receive a reasonable explanation.[2]

Total Reflexion Phenomena.

The use of a steel diffracting edge as an explorer enables us to determine experimentally the extent to which light

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[1] C. V. Raman and K. S. Krishnan, Proc. Roy. Soc., A., Vol. 116, p. 251.

[2] C. V. Raman and I. Ramakrishna Rao, Proc. Phys. Soc., London, Vol. 39, p. 453 (1927).

penetrates from the denser to the rarer medium in the case of total reflexion. As the edge gradually approaches the boundary between the two media, and enters the region in which the superficial wave in the second medium has a sensible intensity, it is seen in the observing microscope to become suddenly luminous. The direction of flow of energy in the superficial wave and its state of polarisation may be determined in this way.[1]

The same paper settles finally a hundred year old controversy regarding the absolute value of the change of phase occurring on reflexion, or in other words with regard to the proper signs to be assigned to the well-known tangent and sine-formulae of Fresnel. For a long time the positive and the negative signs seem to have been used indifferently. However when Lord Kelvin in his famous Baltimore lectures drew attention to what he called the "manifest absurdity" of giving different signs to the tangent formula and the sine-formula "because at very nearly normal incidences the tangents are aproximately equal to the sines, and at normal incidences the two formulae mean precisely the same thing, there being at normal incidence no such thing as a difference between vibrations in, and vibrations perpendicular to, a plane of incidence," the question was supposed to have been finally settled. But with the general acceptance of the electromagnetic theory of Maxwell with its postulate of two light vectors, *viz.*, the electric and magnetic vectors perpendicular to each other and to the direction of propagation, instead of a single light-vector of the classical theory which Kelvin had in his hand, the controversy has been revived. The general convention of the electromagnetic theory that the phase of a light wave can be determined indifferently from the phase of either the electric vector or the magnetic vector supplies the new criterion for the choice of signs; that is to

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[1] C. V. Raman, Trans. Opt. Soc., Lond., Vol. 28, p. 149, (1927).

say, it is only necessary to ensure that at every stage of
propagation of a light-wave—and therefore also when it
suffers reflexion—the electric and magnetic vectors are identi-
cal in phase. In the case of reflexion it happens that the
identity in phase of the two vectors will remain unaltered
by reflexion only when we assign to the Fresnal expressions
opposite signs and not the same sign as has been suggested
by Lord Kelvin.

Brewster's Bands.

Mr. Susilkrishna Datta has continued the investigations
on the explanation of Brewster's bands from the view-point
suggested by Schuster; and in a paper in the Optical Society's
Transactions[1] he discusses the nature of the patterns ob-
tained by the superposition of two systems of Haidinger's
rings when the actual law of spacing of the rings is taken
into consideration.

Liquid Surfaces.

During the year under report, the thesis of Dr. L. A.
Ramdas was published.[2] This deals with the scattering of
light by liquid surfaces. Dr. Ramdas studied experimentally
the surface-scattering by carbon dioxide near the critical
temperature. As the temperature of the liquid is slowly
raised to the critical temperature, the surface scattering
observed at the critical angle from below in the plane of
incidence is found to increase very rapidly to a maximum
value at 31·131°C. beyond which the surface gets too rough
to reflect any light and develops a thick surface layer. The
layer persists till the temperature rises to 31·377°C. during
which interval the transition layer gets thicker and

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[1] S. K. Datta, Trans. Opt. Soo., London, Vol. 28, p. 214 (1927).
[2] L. A. Ramdas, Ind. Jour. Phys., Vol. 1, p. 199 (1927).

thicker and finally fills the whole bulb. On the other hand, approaching the critical temperature from above, the liquid phase does not reappear till 31·131°C.

Measurements have also been published during the year made by Dr. Ramdas[1] on the well-known elliptic polarisation of light reflected from fresh surfaces at the polarising angle. On the basis of Drude's theory of a surface layer of smaller refractive index, the thickness of the layer has been estimated for different organic liquids and is shown to be of molecular dimension.

5. *Magnetic Researches.*

During the year under consideration, an accurate study of the magnetic properties of vapours was undertaken by Mr. V. I. Vaidyanathan. Mention was made in the report last year, of a sensitive apparatus, developed in this laboratory for the study of the diamagnetism of gases.

The investigation was extended to vapours, to see if any change of diamagnetic susceptibility occurred during the transition from liquid to vapour.[2]

Two methods were employed. The first method was, in all essentials, the same as that used for gases and described in the last year's report. The second method utilised the orientative couple exerted on a small symmetrical rod or tube suspended by its centre, in a non-homogeneous magnetic field.

The essential part of the apparatus consists of 3 small tubes attached one below the other and made "astatic" (*i.e.*) if the space round the tubes is a vacuum, then very little orientative force is exerted on the tubes in a magnetic field. These tubes are enclosed in a long vertical chamber, from

[1] C. V. Raman and L. A. Ramdas, Phil. Mag., Vol. 3, p. 220 (1927).

[2] V. I. Vaidyanathan, Phys. Rev., Vol. 30, p. 512, (1927); Ind. Journ. Phys., Vol. 2, p. 185 (1928).

which air could be exhausted and the vapours under investigation let in. The orientative couple on the tubes, in a magnetic field, depends on the magnetic property of the surrounding medium, and causes a twist on the torsion fibre, by means of which these tubes are suspended. The amount of this twist is measured as in galvanometers and the diamagnetic susceptibility of the vapour is compared with that of a known gas.

The experimental difficulties are great but in certain cases, both methods yielded a larger diamagnetic value in the vapour state than in the liquid. For instance, in carbon disulphide and benzene, the molecular diamagnetic susceptibility in the vapour state is 20 to 30% higher than in the liquid state.

Such a result is not altogether surprising, for, similar increase of diamagnetism has been previously observed when a crystal melts to a liquid. In a memoir published by A.E. Oxley in the Philosophical Transactions, these phenomena observed by him, are explained as due to the presence of a large intermolecular field in crystals. In the case of liquids as different from a vapour, the proximity of the neighbouring molecules might cause a distortion of the outer electron orbits, or the molecules might pair themselves to form associated ones. When transformed into a vapour, these intermolecular influences and associations are decreased. The electron orbits, which are fundamentally responsible for diamagnetism are thus possibly increased in size and freer in the vapour than in the liquid. The explanation is not altogether without difficulties, but it affords a reasonable ground for explaining the change which has actually been observed.

6. *Acoustical Investigations.*

Mr. Panchanan Das continued his investigations on the acoustic of the pianoforte, and published a paper in the Indian

Journal of Physics on the energy of a struck string, and showed how its variations with the position of the striking point may be satisfactorily explained. The theory of the elastic pianoforte hammer was also discussed by him in a paper published in the Proceedings of the Physical Society.[1]

Mr. Manindranath Mitra had a paper in our Journal[2] on the generalised law of vibration of the bowed string and its experimental verification.

7. *Pleochroic Haloes.*

Certain minerals such as the micas, hornblende and cordierite when viewed under the polarising microscope show minute particles, surrounding which are concentric rings of varying intensity ; with the rotation of the stage of the microscope, these rings show changes of colour. An exact explanation of their origin long baffled scientists until in 1907 Joly correlated them with the radio-active elements of Thorium and Uranium series and showed from their radial measurements that the haloes were caused by the α-rays given out during the disintegration of the parent elements into the successive members of the two series. Joly and other workers found that while in biotite, the values obtained showed a good agreement with the calculated values those in cordierite had discrepancies in the agreement. This was attributed to the greater sensitiveness of cordierite which resulted in rapid loss of details. Mr. Mahadevan took up the study of the pleochroic haloes occurring in South Indian cordierites.[3] Sections of the mineral were ground in the laboratory and a thorough study of these haloes was made with a polarising microscope, a Zeiss ocular micrometer previously graduated with a diffraction grating being used for the measurements.

[1] P. Das, Proc. Phys. Soc. London, Vol. 40, p. 29, (1927).

[2] M. N. Mitra, Ind. Jour. Phys., Vol. 1, p. 311, (1927).

[3] C. Mahadevan, Ind. Jour. Phys., Vol. 1, p. 445, (1927).

As a result of his investigations, Mr. Mahadevan has shown that the observed radii of the pleochroic haloes in South Indian Cordierite agree well with the theoretical values and that there is no more discrepancy in the values in cordierite than there is in biotite. Incidentally, from the data obtained, the incorrectness of attributing an independent origin to the actinium series was pointed out.

It may be mentioned in passing that this was the first attempt in India to study this well-known radio-active phenomenon in minerals.

8. *A New Synthetic Resin.*

The Chemical laboratory was particularly active during the year. An outstanding feature of the work has been the discovery of a new synthetic hydrocarbon resin by one of the part-time workers, Mr. P. Krishnamurti. The process utilises the cheap commercial article toluene which is first chlorinated and the product then resinified by treatment with suitable reagents. The resin thus obtained resembles natural shellac in most of its properties, with the one exception that whereas shellac dissolves freely in alcohol, the new resin dissolves readily only in benzene or in any of the coal-tar solvents. Judging from its properties, it bids fair to take its place along with shellac in the electrical and allied industries.

Another interesting piece of work carried out by the same worker was a study of the interaction between benzoylaceto-nitrile and various organic bases in the presence of salicylal-dehyde as catalyst. The results of the investigation were published in the J. C. S. (June). It was found to be an entirely new kind of addition reaction which could be utilized to determine the mobility of the hydrogen atom of the amino group in organic bases. Several amines were studied and subsequently another paper on the subject was communicated to the J.C.S. for publication.

Mr. Mahadevan conducted in the Chemical Laboratory several analyses of chromite, manganese and other ores collected by him during his field work in Singhbhum district. During the latter part of the year, more than twenty dry assayings were carried out by him in the muffle furnace for gold and silver from samples of rocks and sands obtained from Bihar.

Mr. S. Venkateswaran of the Government Test House, Alipur, worked in the Chemical Laboratory of the Association and carried out a series of measurements of the compressibilities of aqueous solutions of the fatty acids. Tyrer's method was employed.

9. *List of Papers published during the year 1927.*

INDIAN JOURNAL OF PHYSICS.

VOL. I.—PART III.

1. The Scattering of Light by Liquid Surfaces—By L. A Ramdas.
2. The Molecular Scattering of Light in Aqueous Solutions, Part I—By S. Venkateswaran.
3. Magnetic Double Refraction in Paramagnetic Gases —By K. S. Krishnan.
4. A Relation Between the Specific Heat, Thermal Expansion, and velocity of Sound in Liquids—By B. N. Sreenivasaiah.
5. The Generalised Law of Vibration of Bowed Strings— By Manindranath Mitra.

INDIAN JOURNAL OF PHYSICS.

VOL. I.—PART IV.

6. X-Ray Diffraction in Liquids—By C. M. Sogani.
7. The Molecular Scattering of Light in Aqueous Solutions, Part II—By S. Venkateswaran.

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8. On Fluctuations of Dielectric Constant in Liquids and Theories of Molecular Scattering of Light— By K. R. Ramanathan.

9. The Energy of a Struck String—By P. Das.

10. Pleochroic Haloes in Cordierite—By C. Mahadevan.

INDIAN JOURNAL OF PHYSICS.

Vol II.—Part—I.

11. Relation of Tyndall-Effect to Osmotic Pressure in Colloidal Solutions—By C. V. Raman.

12. The Scattering of Light by Liquids at High Temperatures—By S. Ramachandra Rao.

13. Scattering of Light by Aromatic Compounds—By A. N. Banerjee.

14. Determination and Discussion of Light-Scattering Data for 10 Gases and 63 Vapours of Organic Compounds—By I. Ramakrishna Rao.

15. Further Studies in X-Ray Liquid-Diffraction—By C. M. Sogani.

Nature.

16. " Magnetic Double Refraction "—by C. V. Raman and I. Ramakrishna Rao.

17. " X-Ray Diffraction in Liquids"—by C. V. Raman and C. M. Sogani.

18. " Optical Behaviour of Protein Solutions "—by C.V. Raman.

19. " X-Ray Diffraction in Liquids "—by C. V. Raman and C. M. Sogani.

20. " The Maxwell-Effect in Liquids "—by C. V. Raman and K. S. Krishnan.

21. " Thermal Degeneration of the X-Ray Haloes in Liquids "—by C. V. Raman.

22.   " Thermodynamics, Wave-Theory and the Compton-
      Effects "—by C. V. Raman.

Proceedings of the Royal Society.

23.   "Magnetic Double-Refraction in Liquids.   Part I—
      Benzene and its Derivatives "—by C. V. Raman
      and K. S. Krishnan.
24.   " The Magnetic Anisotropy of Crystalline Nitrates
      and Carbonates "—by K. S. Krishnan and C. V.
      Raman.
25.   " The Diffraction of Light by Metallic Screens "—
      by C. V. Raman and K. S. Krishnan.
26.   "A Theory of Electric and Magnetic Birefringence
      in Liquids—by C. V. Raman and K. S. Krishnan.

The Philosophical Magazine.

27.   " Thickness of the Optical Transition Layer in
      Liquid Surfaces "—by C. V. Raman and L. A.
      Ramdas.
28.   " Electric Double-Refraction in Relation to the
      Polarity and Optical Anisotropy of Molecules,"
      Part I—Gases and Vapours—by C. V. Raman and
      K. S. Krishnan.
29.   „   „   Part II—Liquids—by C. V. Raman
      and K. S. Krishnan.
30.   " The Molecular Scattering of Light in Binary
      Liquid Mixtures "—by C. V. Raman.

Comptes Rendus.

31.   " La constante de birefringence magnetique du ben-
      zene "—by C. V. Raman and K. S. Krishnan.

The Physical Review.

32. "On the Magnetic Susceptibilities of Vapours of Organic Liquids "—by V. I. Vaidyanathan.

Proceedings of the Physical Society of London.

33. " Diffraction of Light by a Transparent Lamina"— by C. V. Raman and I. Ramakrishna Rao.

34. " Theory of the Elastic Pianoforte Hammer "—by Panchanan Das.

Transactions of the Optical Society of London.

35. "Huygens' Principle and the Phenomena of Total Reflexion "—by C. V. Raman.

36. " On Brewster's Bands, Part II "—by Sushil Krishna Datta.

Journal of the Optical Society of America.

37. "The Scattering of Light in Amorphous Solids "—by C. V. Raman.

The Journal of Physical Chemistry.

38. " Compressibilics of Aqueous Solutions of some Fatty Acids "—by S. Venkateswaran.

Journal of the Chemical Society of London.

39. " The union of Benzoyl Acetonitrile with Organic Bases in the Presence of Salicylaldehyde, Part I, by P. Krishnamurti and B. B. Dey.—

PART II.

ADMINISTRATIVE REPORT.

10. *Our Research Workers.*

Facilities for research work in our laboratory were given during the year 1927 to 36 research workers, of whom 23 worked whole-time during the period of their stay at Calcutta and 13 were part-time workers. The different provinces of India were all represented, with the exception of Bombay, Punjab and Behar. The scope of the problems under investigation by them will be sufficiently indicated by the preceding sections of the report, and by the papers appearing in our Journal.

11. *Lecture Arrangements.*

Regular courses of lectures in Physics and Chemistry for the benefit of students were delivered at the Association with the aid of our apparatus and demonstrators.

Your Honorary Secretary delivered numerous public lectures on the scientific work done at the Association during his tours in different parts of India. In the year 1927, he visited and lectured at Benares, Rangoon, Madras and Bangalore. Special lectures were also delivered at the invitation of various public institutions in the city of Calcutta.

12. *Laboratory Equipment.*

The following additions have been made during the year to our stock of Apparatus :—

1. One Gaiffe's Mercury Interrupter.
2. One oil-cooled Transformer for X-ray work.
3. 3 Weston Voltmeters.
4. 3 Weston Ammeters.

5.   1 Induction Coil.
6.   2 Cenco Hyvac pumps.
7.   16 complete outfits of hanging lamps for laboratory and lecture hall.
8.   One 10 H. P. Motor for workshop.
9.   One Air Liquifying plant including standard Air liquifier, etc., complete with 12 H. P. 440 Volt. D. C. Motor and Starter.
10.   4 Cylinders of the following gases were purchased from the Lightfoot Refrigeration Co:—
       (*a*) one cylinder SO_2 50lb.
       (*b*) one   ,,   Nitrogen gas 80 cft.
       (*c*) one   ,,   Nitrous oxide 1475 gallons.
       (*d*) one   ,,   Hydrogen gas 80 cft.
11.   One Silica condensation pump.
12.   One 1000 C. P. Pointolite Lamp.
13.   2 Milliammeters.

13. *Library and Reading Room.*

The following publications were subscribed for as usual :—

1.   The Scientific American.
2.   Nature.
3.   Science Abstracts, A and B.
4.   American Journal of Science.
5.   Philosophical Magazine.
6.   Astrophysical Journal.
7.   Chemical News.
8.   Proceedings of the Royal Society, A.
9.   Proceedings of the Royal Institution of Great Britain.
10.   Transactions of the Royal Society, A.
11.   Physical Review.
12.   Physikalische Berichte.
13.   Zeitschrift fur Physik.
14.   Annalen der Physik.

15. Physikalische Zeitschrift.
16. Journal of the American Chemical Society.
17. Journal of Physical Chemistry.
18. Proceedings of the National Academy of Sciences, Washington.
19. Zeitschrift fur Kristallographie.
20. Zeitschrift fur Physikalische-chemie.
21. Annales de Physique.
22. Comptes Rendus.
23. Chemical Abstracts.
24. Revue de Optique.
25. Science Progress.

We have to acknowledge with thanks the presentation of journals and periodicals in exchange for our Proceedings from the following societies and institutions :—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Akademie der Wissenschaften, Leipzig.
8. Franklin Institute.
9. South African Association for the Advancement of Science.
10. The Prussian Academy of Science, Berlin, Germany.
11. University of Philadelphia.
12. The Physical Society of France.
13. Bureau of Standards.
14. University of Iowa.
15. University of Calcutta.
16. Calcutta Mathematical Society.
17. Indian Chemical Society.
18. Reale Academia Nazionale Dei Lincei, Rome.

19. Societe de Physique et D' Historie—Naturelle, Geneve.
20. Journal of the Chemical Society, London and British Chemical Abstracts, Presentation from Rai Bahadur Chunilal Bose.
21. Bayerischen Akademie der Wissenschaften, Munchen.
22. Der Gesselschaft de Wissenschaften, Gottingen.
23. University of Allahabad.
24. Ariculture Institute of Pusa.
25. Asiatic Society of Bengal.
26. Indian Institute of Science, Bangalore.
27. The Geological Survey of India.
28. Indian Mathematical Society, Presentation from Prof. C. V. Raman.
29. Academy of Sciences, Cracow.
30. University de la Brano.
31. University of Brazil.
32. Academy of Sciences, Leningrad, Russia.
33. University of Durham.
34. Royal Academy of Sciences, Amsterdam.
35. Imperial Academy, Tokyo, Japan.
36. De la Facultad de Sciences, La Plata.
37. Royal Meteorological Society, London.
38. University of Frankfurt a. Main.
39. Royal Dublin Society.
40. Tohoku Imperial University.
41. Institute of Physical and Chemical Research, Japan.
42. Royal Academy of Sciences, Copenhagen.
43. Kodaikanal Observatory.
44. College of Science, Kyoto, Japan.
45. National Research Council, Japan.
46. Academy of Sciences, Vienna, Austria.
47. Proceedings of the Royal Society of London, B. Presentation from Prof. C. V. Raman.

48. Transactions of the Royal Society,—B. Presentation from Prof. C. V. Raman.
49. Societe Chimique, Zagreb, Yougoslave.
50. Hungary University.
51. Ungarische Akademie, Budapest.
52. American Chemical Society.
53. Della Societa Italiana Di Fisica.
54. Societe De chimie-physique, Paris.
55. Mathematikai Es Physikai Akademia, Budapest.
56. National Physical Laboratory of London.
57. Nederlandsch Tijdschrift Voor Natuurkunde.
58. Physical Society of London.
59. Comite de Reveu generale des Sciences.
60. Editor of " Physique Theorique."
61. University of Upsala.
62. University of California.
63. Wissenschaftlische Veroffentlichungen aus dem Siemens-Konzern.
64. Societe Polonaise de Physique, Warszawa.
65. Societe Vaudoise des Sciences Naturelles-Lausanne.
66. United States Department of Agriculture.
67. Nizamia Observatory.

The following books were purchased during the year :—

1. Cloud Studies—A. W. Clayden.
2. The Structure of the Atom—Andrade.
3. Introduction to Contemporary Physics—Karl K. Darraw.
4. Introduction to Theoretical Physics, Vols. I and II—Arthur Haas.
5. Monographs on Physics—E. Cunninghum.
6. A Survey of Physics—Max Planck.
7. High Vacua—Kaye.
8. The Principles of Relativity—A. Einstein and others.
9. Space and Time—Borel.

19

10. Space, Time and Matter—Hermann Weyl.
11. German Science Reader—W. H. Wail.
12. A Short History of Physics—H. Buckley.
13. Abhandlungen Zur Wellenmechanik—E. Schrödinger.
14. Struktur Der Materie (1) E. Back und Lande.
15.   Do.   (2) Max Born.
16.   Do.   (3) J. Franck und P. Jordon.
17.   Do.   (4) F. Hund.
18.   Do.   (5) G. V. Hevesy.
19. Three Lectures on Atomic Physics—A. Sommerfeld.
20. Vortrage uber Die Kinestische Theorie Der Materie und Der Elektrizitat—M. Planck.
21. Treatise on Natural Philosophy—Thomson.
22. Electrical and Optical Wave Motion—H. Bateman.
23. A Treatise on Electricity—F.B. Pidduck.
24. Storage Batteries—George Wood Vinal.
25. Coils and Magnet Wire—Charles R. Underhill.
26. Applied X-Rays—George L. Clark.
27. X-Rays and Crystal Structure—W. H. Bragg.
28. X-Rays—Maurice De Broglie.
29. Ions, Electrons and Ionizing Radiations—J.A. Crowther.
30. The Evolutions and Development of the Quantum Theory—N. M. Bligh.
31. X-Rays and Electrons—A. H. Compton.
32. Practical Handbook on Electro-plating—Publishers W. Canning and Co., Ltd.,
33. The Electron—Millikan.
34. Direct Circuit, Electrical Engineering—J. R. Barn.
35. Electricity and Magnetism—Starling.
36. Electricity and Magnetism—J. H. Jeans.
37. Ions, Electrons and Ionising Radiations—J.A. Crowther.
38. Thermionic Phenomena—J. R. Clarke.

39. A Condensed Collection of Thermodynamic Formula
—P. W. Bridgman.
40. The Theory of Sound, Vols. 1 and 2—Lord Rayleigh.
41. Thermodynamics—C. N. Hinshelwood.
42. Treatise on Thermodynamics—Max Planck.
43. Sidelights on Relativity—Albert Einstein.
44. Molecular Spectra in Gases—National Research
Council Bulletin, Vol. 11. Pt. 3.
45. Theory of Light—Preston.
46. Treatise on Practical Light—Wood.
47. Treatise on Practical Light—R. S. Clay.
48. The Principles of Sound Signalling—M. D. Hart
and Smith.
49. Sound—E. G. Richardson.
50. Logarithmic Tables—Frank Castle.
51. Elementary Vector Analysis—C. E. Weatherburn.
52. Advaced Vector Analysis—Weatherburn.
53. The Theory of Elliptic Functions—Hancock.
54. Outline of Wireless—Turner.
55. The Classification of Flowering Plants, Vols. 1 and 2
—Alfred Barton Rendles.
56. Mannual of Petrographic Methods—Albert
Jobanson.
57. Gmelins Handbuch der anorganischen chemie No.
19.
58. Do. Do. Nos. 20, 2 and 6.
59. Chemische Krystallographic—P. Groth. (Teil 1
to 5).
60. The Encyclopaedia Britannica—13th Edition—1, 2,
3 Vols.
61. Proceedings of the Optical Convention, 1926, Pts. 1
and 2.
62. A French-English Dictionary for Chemists—Austin
M. Patterson.
63. A German-English Dictionary for Chemists—Do.

64. International Critical Tables—Vols. II.

65. Handbuch der Physik Bds., I, II, VII, IX, X, XI, XIV, XV, XVII, XXII, XXIII, XXIV, XXI, V, VIII, XVI, XII.

66. Indian Year-Book—1926.

67. Landolt-Bornstein-Physikalische—Chemische Tabellen.

68. Tables Annells Internationales de Constantes Dennees Nameriques, Vols. I, II, III, IV (Pts. I and II), V, (Pts. 1 and 2), VI (Pt. 1).

69. Organic Chemistry—Pts. 1, 2 and 3—J. B. Cohen.

70. Recent Advances in Organic Chemistry—Alfred W. Stewart.

71. A Text-book on Organic Chemistry—Julius Schmidt.

72. Recent Advances in Physical and Inorganic Chemistry—Alfred W. Stewart.

73. Cornell University Lectures—Ernest Cohen.

74. A Comprehensive Treatise on Inorganic & Theoretical Chemistry—1, 2, 3, 4, 5, 6 and 7—J. W. Mellor.

75. Photo-Synthesis—Spoehr.

76. Catalysis in Theory and Practice—Rideal & Taylor.

77. Practical Physical Chemistry—Alexander Findlay.

78. The Determination of Hydrogen Ions—W. Mansfield.

79. Natural Organic Colouring Matters—A. G. Perkin and A. E. Everest.

80. Organic Compounds of Arsenic and Antimony—G. T. Morgan.

81. Vat Colours—J. F. Thorpe and C. K. Ingold.

82. Chemical constitution of the Proteins—R. H. Aders Plimmer.

83. Dyestuffs Derived from Pyridine, etc.—J. T. Hewitt.

84. Colloid Chemistry—Pauli.

14. *Workshop.*

The Workshop of the Association continued to function as a valuable auxiliary to our Research Laboratories and the mechanics turned out the following appliances :—

1. Brass Sockets for Oxygen Cylinders—3.
2. Copper Condensers for measuring dielectric capacity of gases by oscillating valve method—2.
3. Adjustable Electromagnet—1.
4. Mild steel pole—pieces for two big Electro-magnets, adjustable—4.
5. Glass vessels on brass frame—4.
6. Fitting up two posts and 4 Wall Iron Brackets for Electric Installation.
7. Oscillating Crystal spectrometer—1.
8. Adjustable table for crystal—1.
9. Heating arrangements for liquid cells for X-ray camera.
10. Brass X-ray camera—1.
11. Lead X-ray camera—3.
12. X-ray Shearer Tubes—3.
13. X-ray camera box—5.
14. Thin brass cells for X-ray camera—6.
15. Wire Resistance in frame—6.
16. Arrangement for Rotating hot carbon Pencil—1.
17. Galvanized tanks for X-ray coil—6.
18. Ebonite posts for X-ray coils—16.
19. X-ray Tube stands—4.
20. Zinc water-vessels—2.

Besides the above apparatus, a large number of repairs and small fittings for Laboratory and for Electric installations were made.

15.　*Financial Statement.*

On the 31st December, 1927, the Association had in the custody of the Imperial Bank of India, Government Securities to the nominal value of Rs. 1,87,800, in the General Fund, Rs. 17,000 in the Ripon Professorship Fund, Rs. 1,000 in the Victoria Professorship Fund, Rs. 21,500 in the Maharajah Cooch-Behar Professorship Fund, Rs. 1,000 in the Hare Professorship Fund, Rs. 500 in the Nikunja-Garabini Prize Fund, Rs. 600 in Jatindrachandra Prize Fund, Rs. 500 in the Woodburn Medal Fund, Rs. 3,000 in the Dr. Sircar Research Medal Fund, Rs. 9,000 in the Joykissen Medal Fund, a floating balance in the Bank of Rs. 689-3 and a cash balance in the office of Rs. 49-5-6, amounting in all to Rs. 2, 42, 638 8-6.

On the 31st December, 1926, the Association had in the custody of the Imperial Bank of India, Government Securities to the nominal value of Rs. 2,35,400 in the General Fund, Rs. 6,000 in the Ripon Professorship Fund, Rs. 500 in the Nikunja-Garabini Prize Fund, a floating balance in the Bank of Rs. 2,391-15-5 and a cash balance in the office of Rs. 523-5-6, amounting in all to Rs. 2,44,815-4-11.

A copy of our balance sheet and the statement of Receipts and Expenditure during the year is attached to the report.

16.　*Acknowledgments.*

The thanks of the Association are due to the Honorary Engineer, Rai Krishnachandra Banerjee Bahadur, Babu Bhabadev Chatterjee, Babu Bhutnath Chakravarti, the Honorary Legal Advisers, Babu Jatindranath Basu and Babu Nirmalchunder Chunder, to the Honorary Secretary, Prof. C. V. Raman and to the Honorary Assistant Secretaries, Babu Jyotischandra Pal and Babu Asutosh Dey, for their gratuitous services.

STATEMENT OF ACCOUNTS FOR 1927

RECEIPTS.

	Rs.	As.	P.
Subscriptions	348	0	0
Donations	3,336	9	0
Rent from shops	4,332	0	0
Miscellaneous Receipts	1,209	6	3
Dr. Sircar Memorial Fund	1,405	4	0
Building Fund	6,160	0	0
Government of India Grant	20,000	0	0
Sale of Bulletins, etc.	1,216	11	10
Interest a/c General Fund	8,067	10	0
„ „ Ripon P. Fund	190	0	0
„ „ N. G. Prize Fund	17	8	0
„ „ Jatindrachandra Prize Fund ...	19	4	0
„ „ Woodburn Medal Fund ..	17	8	0
„ „ Dr. Sircar Research Medal Fund	105	0	0
Suspense account	193	11	0
Provident Fund	562	1	6
P. O. Savings Bank—withdrawn	1,627	0	0
Opening Balance on 1st January, 1927 : Bank	2,391	15	5
Office ...	523	5	6
Rs.	51,722	14	6

Examined and found correct

SAHA AND MAJUMDER,

Government Certified Auditors

PAYMENTS.

	RS.	AS.	P.
Commission a/c General Fund ...	25	15	0
„ „ Ripon Prof. fund	1	6	0
„ „ Nikunja G. Fund	0	3	0
Establishment Account ...	7,485	9	3
Municipal Tax	1,094	0	0
Electric charges	1,700	5	0
Gas charges	445	13	6
Building Repairs	625	5	0
Furniture Account	941	15	3
Laboratory charges	5,177	15	6
Workshop charges	1,451	11	3
Postage and Telegrams ...	646	5	0
Printing charges	3,360	15	0
Miscellaneous charges ...	3,711	9	9
Telephone charges	169	3	3
Research Scholarships ...	4,187	8	0
Institute contribution to Prov. Fund	120	15	6
Scientific Instrument Account G. Fund	11,959	9	3
Library Account	4,174	1	0
Electric Installation account ...	2,481	7	6
Gas and Water Fittings ...	115	8	0
Vizianagram Fund	150	0	0
Provident Fund	222	9	0
P. O. Savings Bank Deposits ...	332	14	0
Suspense Account	223	11	0
Workshop Instruments Account ...	177	15	0
Closing Balance on 31st December, 1927			
at Imperial Bank	689	3	0
at Office ...	49	5	6
Rs.	51,722	14	6

C. V. RAMAN,
Honorary Secretary.

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ASSETS.

			Rs.	AS.	P.
Land and Old Building	...	...	31,680	11	9
Lecture Hall and Gallery	...	...	23,465	5	3
Vizianagram Laboratory	...	...	40,900	14	0
Observatory Room ...	...	...	3,320	9	9
Range of Shops (East)	...	...	2,516	10	9
Range of Shops (West)	...	...	2,308	5	0
Servants' Quarters ...	...	...	1,024	0	0
Durwan's Quarter ...	...	...	303	13	9
Scientific Instruments (K. K. Tagore Fund) ...			25,000	0	0
Scientific Instruments (General Fund)		...	65,794	1	2
Botanical Instruments	...	...	2,329	6	0
Workshop Instruments	...	...	9,792	13	3
Tools and Implements	...	...	203	3	3
Library Account ...	...	...	33,234	12	4
Furniture Account ...	...	...	9,975	0	0
Suspense Account ...	...	...	40	0	0
Government Securities—3½ per cent. G. Fund			1,87,800	0	0
,, ,, Ripon Prof. Fund ...			13,000	0	0
,, ,, Victoria P. Fund ...			1,000	0	0
,, ,, Maharajah Coochbehar P. Fund ...			21,500	0	0
,, ,, Hare P. Fund ...			1,000	0	0
,, ,, N. G. P. Fund ...			500	0	0
,, ,, Jatindrachandra P. Fund			600	0	0
,, ,, Woodburn M. F. ...			500	0	0
,, ,, Dr. Sircar R. M. P....			3,000	0	0
,, ,, R. P. Fund 3 per cent.			4,000	0	0
,, ,, Joykissen M. F. ...			9,000	0	0
Balance at P. O. Savings Bank ...		...	422	12	4
Imperial Bank ...		...	689	3	0
Office ...	...	...	49	5	6

Rs.	4,94,950	15	1

C. V. RAMAN,
Honorary Secretary.

	LIABILITIES.	Rs.	As.	P.
General Fund	...2,50,520	13	1
Investment Reserve Fund ...	... 60,895	0	0
Depreciation Reserve Fund *Property*	... 45,520	6	3
,, ,, ,, *Instruments*	... 43,119	7	8
,, ,, ,, *Furniture*	... 13,234	12	4
,, ,, ,, *Library*	... 3,325	0	0
Provident Fund	... 2,200	9	10
Victoria Prof. Fund	... 1,000	0	0
Ripon Prof. Fund	... 17,000	0	0
Maharajah Cooch-Behar P. Fund ...	... 21,500	0	0
Hare Professorship Fund ...	... 1,000	0	0
Nikunja-Garabini Prize Fund ...	... 500	0	0
Jatindrachandra P. Fund ...	... 600	0	0
Joykissen Medal Fund ...	... 9,000	0	0
Woodburn ,, ,, ...	... 500	0	0
Dr. Sircar Research Medal Fund ...	... 3,000	0	0
Dr. Sircar Memorial Fund ...	... 13,685	12	3
Vizianagram Fund	... 40	0	0
Building Fund	... 6,160	0	0
Dr. Sircar Research Medal Fund Interest ...	630	0	0
Ripon Prof. Fund Interest	491	2	3
Nikunja-Garabini Fund Interest	265	6	2
Woodburn Medal Fund Interest	176	8	0
Jatindrachandra P. Fund Interest... ...	123	11	0
Joykissen Medal Fund Interest	339	0	0
Government of India Grant	123	6	3

Rs.   4,94,950 15 1

We have examined the above B/sheet with the books and vouchers and found it correct. The special features of this B/sheet are (1) Furniture has been shown on the B/sheet, (2) Depreciation has been provided for Property, Instruments, Furniture and Library, (3) A reserve has been created for the heavy depreciation of Securities, and (4) the Investments relating to the different Funds have been separated and ear-marked.

SAHA AND MAJUMDER,
Government Certified Auditors.

On the Nature of Dextrin, Gelatin and Sodium Oleate Solutions as revealed by X-ray Diffraction

By

P. Krishnamurti.

(Plates XIV, XV and XVI.)

Abstract.

This is a continuation of the work on the diffraction of X-rays by sugar solutions which are typical crystalloids (Krishnamurti, Ind. Jour. Phys., 3, ii, 209). The study has now been extended to semi-colloidal and colloidal solutions, where the state of molecular aggregation has formed the subject of much speculation. Dextrin, gelatin and sodium oleate solutions were examined both in the solid state and in their solutions at different concentrations. It was found that dextrin solutions give patterns similar to those of the sugars, with the only difference that might be expected if the molecules were much bigger than those of canesugar. The patterns for the dextrin solutions resembled more the patterns for glucose than for levulose, which can be naturally expected since the product of hydrolysis of dextrin is only glucose. Gelatin solutions gave patterns similar to those of dextrin, but the molecules in this case ought to be even bigger than those of dextrin. On the other hand, sodium oleate solutions

behaved quite differently, the solute giving rise to a ring of its own even in fairly dilute solutions.

Dextrin, in dilute solutions, gave rise to the gaseous scattering at small angles, but the extent of the diffraction disk in a 1:1 solution was much smaller than in canesugar, and the molecular spacing correspondingly larger. The molecular weight calculated from the extent of the gaseous scattering by means of the Bragg formula comes to about 600, a value which is not improbable.

Gelatin was not examined at concentrations higher than 1:1 by weight, since the solutions became too viscous. At this and at greater dilutions, it also shows the gaseous scattering at small angles, the extent of the scattering being smaller than in dextrin. When calculated as mentioned above, its molecular weight comes to about 3,000. It is shown that this method will give only the lowest value for the molecular weight when the substance consists of a mixture. The values obtained for highly purified samples of gelatin by other methods are roughly of the same order.

In the case of sodium oleate solutions, the maximum concentration examined was 1:3, and even here the solution was very viscous. At this concentration and at the next one (1:5), it shows a separate ring just below the water ring, of practically the same size as for the powder, though more diffuse. This persists even in concentrations down to 1:10, though it becomes indistinct and exists only as a general scattering after a concentration of 1:7. This ring is explained as due to the presence of big groups or micelles of sodium oleate in the solution which contain several simple molecules arranged parallel to one another as in any long-chain compound (e.g., oleic acid). This is in conformity with the low osmotic pressure exerted by the soap solutions, and with the observations of McBain and his co-workers. The constancy in size of the ring in the solutions as compared to that in the solid is similar to that observed by Katz when sodium palmitate swells in 20% trichlorethylene. Another feature in the diffraction patterns of the soap solutions is the existence of a gaseous scattering at small angles, and a general scattering inside the water halo at all concentrations, especially in dilute solutions. The extent of the gaseous scattering gives the average dimension for the sodium oleate molecule, which agrees fairly with that calculated from its molecular weight and density, and hence may be due to single molecules of sodium oleate or to oleate ions which are present in all the solutions. The general scattering is probably due to sodium ions and also to hydroxyl ions produced by hydrolysis. There is also an excess of scattering directly adjoining the

central spot, which may probably be due to big groups of 'ionic micelles' described by McBain. Work on starch gels and on soap sols, gels and curds is in progress.

The patterns for the powder in the case of gelatin and starch showed, in addition to the rings at larger angles, a fairly intense ring at very small angles. This has been overlooked by the previous observers, probably because the central beam was not cut out in their experiments.

Theoretical.

In the previous communications dealing with X-ray diffraction in aqueous solutions, the present author arrived at some general conclusions regarding the distribution of the dissolved molecules in a solution.[1,2] For instance, in the case of dilute solutions of canesugar, levulose or glucose, it was shown that the molecules were distributed at random in the solution just as a gas, giving a pattern which showed in addition to the water ring, a large amount of scattering at small angles to the primary beam. Moreover, as the concentration of the solution increased beyond a certain limit, the scattering round the central spot diminished in intensity, and the diffraction disk gave place to a well-defined ring. It was also found that the spacing corresponding to the outer edge of the diffraction disk at a concentration of about 1:1 by weight, gave an approximate value for the size of the dissolved molecule. Thus, canesugar which is about twice as heavy as glucose or levulose, showed a gaseous scattering which was smaller in area, and more intense than in either of the latter at the same dilution. In the light of these new observations regarding the disposition of the molecules in solutions of crystalloids, it was thought that a similar study of semi-colloidal and

[1] Krishnamurti, Ind. Jour. Phys., 2, iv, 501 (1928).
[2] Krishnamurti, Ind. Jour. Phys., 3, ii, 209 (1928).

colloidal solutions would show definitely in what manner the molecules or groups of molecules are distributed in their aqueous solutions.

Many colloids and colloidal solutions have been examined with monochromatic X-rays by the method of Debye and Scherrer. [3] The most important observation in this connection is the difference in the spectrograms of precipitated and colloidal preparations of gold and silver found by Scherrer. The colloidal material was prepared from the commercial sols protected by gelatin, the disperse phase of which was separated and examined as a dry powder. In both cases line-spectra were obtained, and the rings in the finely-divided gold appeared in the same places as in the coarsely-crystalline one, but differed from it in being broader. Recently, Bjornstahl [4] has used a method in which the sol is allowed to flow through a fine cylindrical jet in the path of the X-ray beam. The results obtained by him are in conformity with those obtained by Scherrer, that the particles in most sols are crystalline in nature, and possess the same crystal lattice as the bigger crystals.

From the breadth of the spectral lines, it has been found possible to calculate the average size of the particles according to the formula,

$$B = 2 \sqrt{\frac{\log_e{}^2}{\pi}} \cdot \frac{\lambda}{D} \cdot \frac{1}{\cos\frac{\theta}{2}} + b,$$

where B is the angular breadth of the halo up to where the intensity has fallen to half the value, b the minimum breadth of the halo determined by the dimensions of the X-ray beam and the column of powder, and D, the average thickness of

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[3] Scherrer, Zsigmondy's Kolloidchemie, 3rd Ger. Edn., p. 387.

[4] Bjornstahl, Inaugural Dissertation, p. 158 (Uppsala, 1924).

the crystal parallel to the cubic axis. Scherrer obtained a value of about 18·6 A.U. for a colloidal gold preparation by the above calculation, showing that the particle of the colloid could contain only about 4—5 of the unit cubes of length 4·07 A.U. The size of the particle determined from osmotic pressure was approximately the same, being about 16 A.U.

In addition to these lyophobic colloids, many organic lyophilic ones have also been examined by means of X-rays. These comprise mainly of gelatin, starch, cellulose and allied substances. [5] Gelatin has been found to give two flat maxima in addition to a general scattering. This was taken to be evidence for the existence of two different substances in gelatin. Starch gave rise to definite crystal interference rings, the crystals being however very small. [6] Ramie gives the characteristic fibre diagram, due to the parallel arrangement of the constituent fibres.

The ease of lyophilic sols which are not coagulated by the passage of X-rays has not yet been fully studied. The most prominent work in this field is due to Katz[7] who has investigated the phenomenon of swelling by the X-ray method. He finds that when substances like cellulose, hydrate celluloses and silk-fibroin swell in water, the imbibition must be intra-micellar since the X-ray diffraction rings do not vary in size before and after swelling. In another class of substances represented by inulin, he finds that the substance shows an imbibition which goes for the greater part into the crystal lattice. The rings are smaller in size for the swollen than for the dry substance. The change in dimensions in the case of inulin was 8—11% and that calculated if all the water had entered the crystal lattice and if this had been isotropically enlarged, was also 11%. Hence he concluded that "in

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[5] Scherrer, *loc. cit.*

[6] Scherrer, *loc. cit.*

[7] Katz, Proc. Roy. Soc. Amster., 27, 505 (1924,).

  Also Katz and Mark, ., ., 27, 520 (1924).

inulin the inbibition water goes for the greater part into the crystal lattice and enlarges this in the same degree as the visible dimensions increase (swell)." On the other hand, chitin in water and sodium palmitate in 20% trichlorethylene showed the rings in almost identical positions in the two cases, and hence were assigned to the same group as cellulose and fibroin. Accordingly, he came to the conclusion that imbibition can take place either intermicellarly or intermolecularly, depending on the nature of the substance.

Among semi-colloids, soap solutions have been studied from several points of view by McBain and his co-workers,[8] who have shown that soap belongs to a new class of substances called ' colloidal electrolytes.' They were led to this conclusion mainly by considerations of osmotic activity and conductivity of soap solutions. It was found that a strong solution of a higher soap exhibits only about half the osmotic activity of an ordinary salt, but the conductivity is equal to that of the latter. Hence they concluded that half the conductivity of the soap solution was due to a negative carrier which did not exert appreciable osmotic pressure, and this they regarded as the ionic micelle. Hence the colloidal electrolyte could be regarded as a salt in which one of the ions is replaced by ionic micelles, consisting mainly of aggregated and hydrated fatty ions. The undissociated colloidal electrolyte consists then of neutral micelles. They have also shown that hydrolysis is of negligible significance except in very dilute solutions. Hence, even in dilute solutions of a soap, e.g., sodium oleate, the constituents are (a) neutral colloid, (b) simple sodium oleate molecules, (c) simple oleate ions and sodium ions, (d) ionic micelle. In very dilute solutions, the acid soap separates out through hydrolysis. The following

⁸ McBain and Salmon, J. Amer. Chem. Soc., 42, 426 (1920).

diagram taken from the paper of McBain and Jenkins [9] shows these conclusions clearly:

Constituents of Sodium Oleate Solutions at 18°C

→ Total concentration of solution (Nw)
* Acid soap : 2 Na Ol, Hol
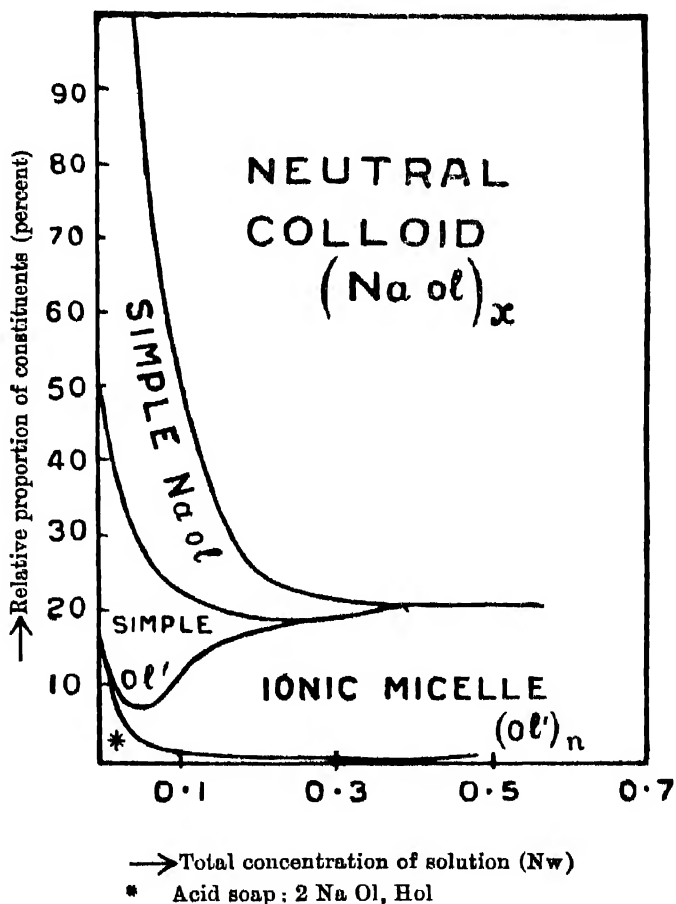
An X-ray investigation of sodium oleate solutions lends support to many of these conclusions, as will be seen later.

It is clear from the short account of the X-ray investigation on colloids given in the preceding pages, that no one has examined solutions of lyophilic colloids in detail by this method. Such work was considered highly important,

[9] McBain and Jenkins, J. Chem. Soc., 121, 2325 (1922).

because we do not as yet know with certainty how the water molecules and colloid particles distribute themselves with reference to one another in the solution. This can happen in either of two ways : either the water is enmeshed between the micelles which may consist of several simple molecules, or the water gets in between the individual molecules. Another point is to find out whether the ultimate molecules are big or small ; in other words, to compute their size with reference to a standard substance whose molecule has known dimensions. A third point will be to find out the changes which take place at different stages of dilution. Finally, the optical behaviour of some colloidal systems, especially the evidence of the ultramicroscope, should be compared with the results obtained by the X-ray method.

The three substances examined in the present investigation, in the solid state as well as in solutions of different concentration, are (1) Dextrin, (2) Ash-free gelatin, (3) Sodium oleate, as representatives of three main classes of substances which can be easily differentiated by the X-ray method. As a result of this investigation, it appears that dextrin* which is a semi-colloid, is very similar to glucose showing an identical behaviour on dilution. The only difference between the two substances seems to be one of the size of the molecule, and the X-ray method shows that dextrin consists simply of a number of glucose molecules united together chemically. Thus it is shown to belong to the class of ordinary crystalloids discussed previously, [10] differing from them only in possessing a higher molecular weight. The case of gelatin is more complex, but it is suggested that it is also molecularly dispersed, consisting of irregularly oriented molecules of different sizes. The molecules are, however, of a much larger size than in dextrin. In the case of sodium oleate, the X-ray pattern shows that in

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[10] Krishnamurti, *loc. cit.*

moderately concentrated solutions micelles do exist, which are made up of several simple oleate molecules arranged almost parallel to one another. In addition, there is also the gaseous scattering at very small angles showing the presence of large groups moving about at random in the solution, together with a large amount of general scattering. In very dilute solutions, a random distribution of simple molecules is evident, as well as the presence of smaller micelles. The big groups of sodium oleate molecules seem to break down partially into smaller groups and simple molecules at a concentration of about 1 : 7. The process, however, is not complete even at 1 : 10 dilution.

It can thus be seen that dextrin belongs to a class of substances which exist in the molecular state in solution, the size of the molecules being however very big when compared to ordinary crystalloids ; gelatin to a class which consists of bigger molecules produced by chemical union of a large and varying number of irregularly oriented molecules, the molecules not breaking down into their constituents even at a large dilution, and finally sodium oleate to a third group which, in solution, is in equilibrium with neutral micelles, ionic micelles and ions. Each case will be considered below in detail.

Dextrin.—Merck's extra pure dextrin, precipitated by alcohol, was used for the experiments. This gives a broad amorphous ring in the solid state, with a certain amount of uniform scattering right up to the central spot. In a dilute solution (1 : 5), in addition to the water ring, there appears the characteristic corona round the centre just as in the dilute sugar solutions, but the extent of the scattering is very small. This scattering increases in intensity in more concentrated solutions (1:3 ; 1:1). At a concentration of 1:1, the water ring has contracted a little just as in the case of glucose solutions. At 2:1, the inner scattering begins to show an increase at the outer edge, while in all the previous cases, it was at a maxi-

2

mum near the central spot and diminished outwards. Even at this concentration, the water ring is quite evident, though very much contracted and diffuse at the edges.

It will be seen from a comparison of the patterns for dextrin with those of canesugar and glucose, that the changes in the patterns on dilution are remarkably alike in all the three cases, and hence could be interpreted in a similar way. The main conclusion is therefore that in a dilute solution of dextrin, the molecules are distributed at random as in a gas, giving rise to a diffraction disk at small angles. As the concentration increases beyond 1:1, there is some amount of destructive interference at very small angles leading to the production of a maximum at a larger angle. The amount of destructive interference is, however, very small, since there is not even partial regularity of arrangement of the molecules as in canesugar or glucose, as can be easily seen from the powder pattern of dextrin, which is only a diffuse amorphous ring with considerable scattering inside the ring. Hence even in concentrated dextrin solutions, there is practically very little arrangement of the molecules, with the result that the inner scattering extends up to the centre, though a slight increase of scattering could be observed at a larger angle.

Another important difference between the patterns for dextrin and the sugar solutions lies in the extent of the gaseous scattering. It is found that at the same concentration, the extent of this scattering decreases from glucose to canesugar, and this further decreases with dextrin. As the spacing of the outer edge of the gaseous scattering at about 1:1 dilution gives an approximate value for the size of the dissolved molecule, it follows that the dextrin molecules are bigger than even the canesugar molecules, since the outer edge of the diffraction disk is smaller in extent, and the spacing correspondingly larger. The following table shows the results clearly :

TABLE I

Concentration of Solution.	Substance.	Extent of gaseous scattering in A.U.	Density of solid.	Mol. wt. observed.	Actual mol. wt.
1:1	Levulose	5·86	1·67	201	180
1:1	Glucose	5·86	1·54	187	180
1:1	Canesugar	7·78	1·59	384	342
1:1	Dextrin	9·88	1·04	604	...
1:3	Gelatin	15·81	1·38	2984	...
1:5	Sod. oleate	7·94	1·04	314	304

Another interesting observation arises when the haloes for dextrin are compared with those for the sugars. It is found that dextrin resembles the patterns for glucose more than those of levulose, especially if the changes in the outer ring with dilution are compared. Up to a concentration of 1:2, the outer rings are almost identical with that of water. But at 1:1, as pointed out previously, the water ring for glucose is slightly smaller than that of levulose, and is more diffuse at the edges. At 2:1, while the water ring has practically vanished for levulose, the ring is still quite prominent in the case of glucose, though smaller in size and more diffuse than at 1:1 dilution. Now, it is found that dextrin at 1:1 and 2:1 dilutions gives the water rings which have contracted and are more diffuse, resembling the glucose patterns to a great extent, and differing from those of levulose. A probable explanation may lie in the fact that dextrin on hydrolysis gives rise exclusively to glucose, and hence is made up of a large number of glucose molecules united together with the elimination of water, since glucose has the formula $C_6H_{12}O_6$ and dextrin $(C_6H_{10}O_5)n$. The factor n can be determined from the approximate value for the molecular weight of dextrin given in Table I. As this comes to about four, we can assume that the dextrin molecule is made up of a similar number of glucose molecules by chemical

union. Since dextrin is a degradation product of starch, a study of starch solutions and gels has been undertaken, and the results will be published shortly.

A great deal of work has been done regarding the changes which take place when starch is converted into dextrin.[11] According to O'Sullivan, when starch is acted on by malt extract at any temperature below 63°C, if the solution be immediately cooled and filtered, the product contains both maltose and dextrin, and he represents the change as follows :

$$(C_{12}H_{20}O_{10})_6 + 4 H_2O \longrightarrow (C_{12}H_{22}O_{11})_4 + (C_{12}H_{20}O_{10})_2$$
$$\text{Starch} \qquad\qquad\qquad \text{Maltose} \qquad\quad \text{Dextrin.}$$
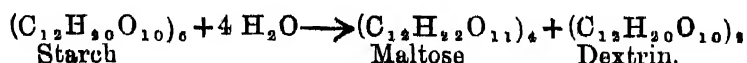
From this equation it is seen that the molecular weight of dextrin comes to about 648, a value very near that obtained by the X-ray method. (Table I.)

Another point which arises in this connection is the reason why in a very concentrated solution of glucose and dextrin (2:1), the water ring should appear prominently, though very much contracted and diffuse at the edges. This point has only been partially dealt with in the previous communication, where the difference was explained as due to the ability of glucose to crystallise with one molecule of water, and hence the probability that more water molecules might attach themselves to it in solution. A simpler method of explaining this difference will be as follows. In a 2:1 solution of levulose, the water molecules which are present in smaller amount can be regarded as distributed at random among the levulose molecules. This results in a general, diffused scattering and there is no maximum. On the other hand, glucose has a decided affinity for water since it can crystallise with water of crystallisation, where the water molecule enters the lattice of the crystal. This idea can be extended to the state of a concentrated solution, since there will be some regularity of

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[11] Thorpe, Dictionary of Applied Chemistry, Vol. II, p. 567 (Longmans, 1905).

DEXTRIN . POWDER

SOLN . 2 : 1

SOLN . 1 : 1

SOLN . 1 : 3

SOLN . 1 : 5

SOLN . 1 : 10
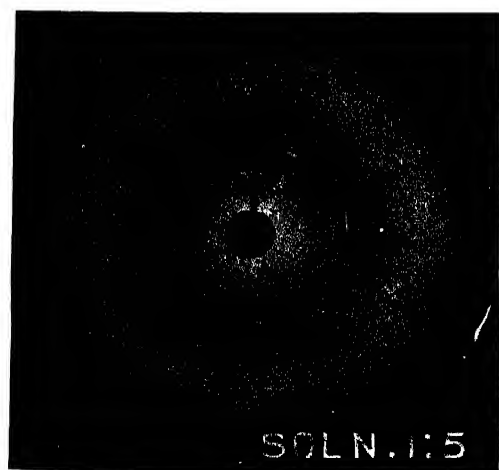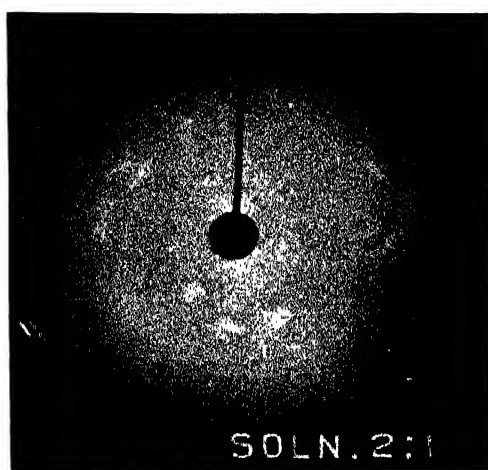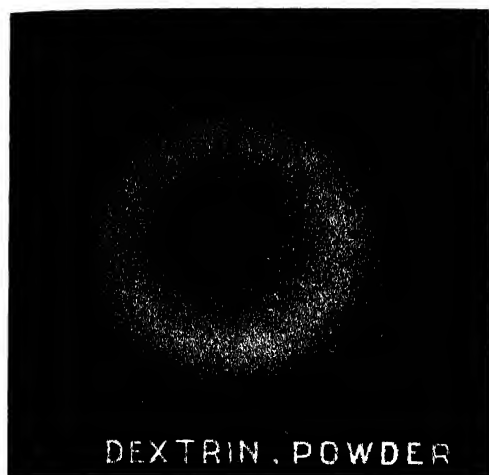
X—Ray Diffraction by Dextrin Solutions

arrangement of the water molecules, and hence a ring is formed. Being separated by glucose molecules, the water molecules are farther apart, and hence the contraction of the ring. The similarity between the glucose and dextrin patterns suggests that some explanation of this type should hold good for dextrin also.

Gelatin.—Specially purified ash-free gelatin of the Eastman Kodak Co., was used in this investigation. Scherrer observed only two flat maxima for the solid gelatin, while Katz finds another sharp ring also.[12] It is now found that there is another ring present at a small angle which could be easily observed since the direct beam was cut out, and hence could not be mistaken as a halation. In dilute solutions, the gaseous scattering is again observed at the centre as in the cases of canesugar and dextrin, in addition to the water ring. The extent of the diffraction disk is however smaller than that for dextrin at the same concentration. The strongest solution examined was 1:1 by weight, and there the inner scattering was intense, the water ring was broader and slightly contracted, and there was some scattering between the ring and the central diffraction disk. The inner scattering diminished in intensity with dilution, and was only faintly perceptible at 1:10. It appears from these observations that the ultimate particles in a gelatin solution are of very large size. The approximate value can be calculated as for canesugar and dextrin from the extent of the inner scattering in a 1:1 solution. If the ultimate particles consist of different sizes, then it is quite evident that the outer edge of the diffraction disk would give only the size of the smallest particles, of which there ought to be a sufficient number. The bigger particles will give a scattering at still smaller angles, and hence if the solution contains a mixture of both varieties, the intensity of the diffraction disk will fall off rapidly from the centre. An

examination of 1 : 1 gelatin solution shows this to be the case. The mol. weight of the smallest particle averages 3000, as can be seen from Table I. Osmotic pressure measurements seem to indicate values for the molecular weight of gelatin ranging from 5500-31,000. It will be noticed that the value obtained by the X-ray method approximates more to the lower limit.

Now let us find out what chemical analysis and the ultramicroscope have to tell us regarding the size of the gelatin molecule. Gelatin results from the hydrolysis of collage or ossein by boiling with water or dilute acids. Hofmeister represents this as follows :[13]

$$C_{102}H_{149}N_{31}O_{38} + H_2O \longrightarrow C_{102}H_{151}N_{31}O_{39}$$

Collagen.   Gelatin.

On heating, gelatin decomposes into various amino acids, *viz.*, glycocoll, leucine, asparagine, glutamic acid, alanine phenyl alanine, αproline and other products. On boiling with water, gelatin gives rise to gelatose, longer boiling especially in the presence of acids yields albumoses and peptones, and finally splits off into the above-mentioned amino acids. Moreover, congo-red, which is only a semi-colloid, has the formula $C_{32}H_{22}N_6S_2O_6Na_2$ with a molecular weight of 696. Hence molecules of much larger size can exist in the case of colloids like gelatin, being produced by chemical union of various amino-acids. In fact, the synthesis of polypeptides of high molecular weight has been accomplished by E. Fischer,[14] who prepared a compound containing as many as 18 amino acids linked together. It has also been found possible to unite together 19 amino acids,[15] the resulting molecule then possessing a molecular weight of 1200 and containing nearly 200

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[13] Allen's Organic Analysis, Vol. VI, (Churchill).

[14] Fischer, Ber. 40, 1764 (1907).

[15] Abderhalden and Fodor, Ber. 49, 561 (1916).

X-Ray Diffraction by Gelatin Solutions

atoms. They show a very close similarity to the natural peptones, when the polypeptides possess a long chain composed of different amino-acid radicles. They are soluble in water, and show the usual reactions for amino-acids. Thus we see that the evidence is strong that the colloid particles in the case of gelatin, may after all be simply molecules of big size, and hence it is possible to regard them from the standpoint of ordinary solutions. X-ray evidence shows that the solutions of gelatin are, as a whole, similar to those of dextrin, if we only assume a larger size for the molecule. The formula proposed for the gelatin molecule by Hofmeister gives a value of 2433, while the X-ray data point to about 3000. The latter value is only approximate, but it suffices to show that the two values are of the same order.

Some preliminary experiments have been conducted with starch powder (Merck's Soluble Starch) and its gels. The solid shows three sharp rings, the first one being very near the central spot. This ring has not been noticed by Ott,[16] probably because he did not cut out the central beam. The different gels show the same gradations in the patterns as gelatin solutions. The inner gaseous scattering is very prominent only very close to the central spot. The extent of the disk is smaller than even with gelatin solutions of the same concentration, showing that the molecule of starch is bigger than that of gelatin. A detailed account of this investigation will be published later.

It will be interesting to note in this connection a recent paper by Svedberg and Chirnoaga[17] on the molecular weight of hemocyanin, by the new method of ultra centrifuging. A molecular weight of 5,000,000 has been obtained for it in a dilute solution.

From osmotic pressure measurements and from the evidence of the ultramicroscope, we can say that the ultimate

[16] Ott, Phys. Zeit., 27, 174 (1926).
[17] Svedberg and Chirnoaga, J. Amer. Chem. Soc., 50, 1399 (1928).

particles of gelatin are of very large size when compared to ordinary molecular dimensions. But it has not been clear till now whether it is molecularly dispersed or whether it forms groups which are only aggregations of simpler molecules. X-ray evidence shows that a gelatin solution consists of molecules of gelatin, the molecules themselves being of very large size, probably formed from simpler molecules by chemical union, and hence not breaking down appreciably on dilution. This case is quite different from that of sodium oleate which forms groups containing several molecules of simple sodium oleate, as will be shown below.

Sodium Oleate.—Kahlbaum's specimen was purified by washing with 95% alcohol and drying. The powder pattern showed three rings as in the case of gelatin, an intense ring surrounding the central spot, another intense ring in the middle and a faint outer ring. In a very dilute solution (1 : 9), the pattern consists of the water ring, a general scattering within the ring, and a region of increased scattering just within the water ring. At the next higher concentration (1 : 7), a very indistinct ring is formed which is just smaller than the water ring, together with a feeble gaseous scattering surrounding the central spot, as well as a general scattering inside the water ring. This becomes more pronounced at a concentration of 1 : 5, when the pattern consists of three distinct regions (1) the water ring, (2) the ring due to sod. oleate, (3) a gaseous scattering extending up to the central spot. The water ring is more intense than the ring due to sod. oleate. The highest concentration examined was 1 : 3, where all the effects found in 1 : 5 solution were present. The sod. oleate ring was stronger and more clearly defined, which was of practically the same size as that in the solid. The inner gaseous scattering was also very prominent. Higher concentrations were not examined since the solution became too viscous and difficult to work with. In all the cases examined, the soap solutions were made optically clear by

SOD. OLEATE POWDER

SOLN.1:3

SOLN.1:5

SOLN.1:7

SOLN.1:9

WATER.
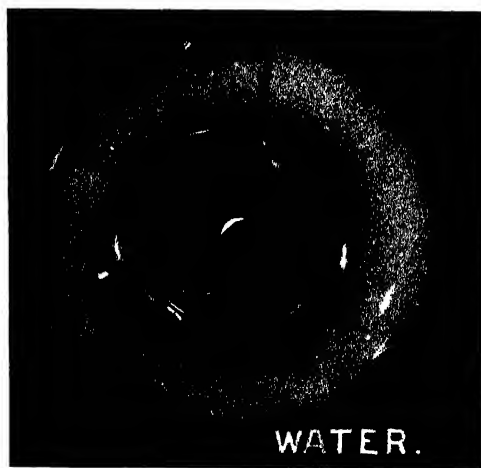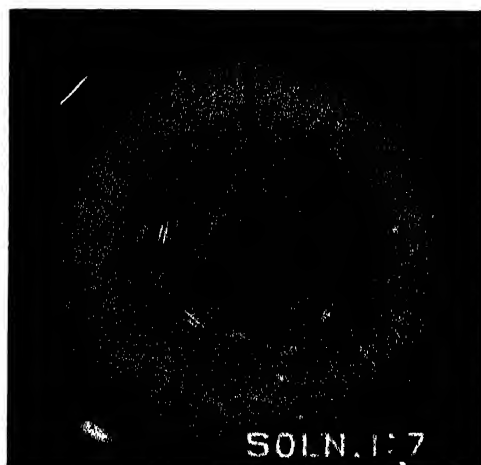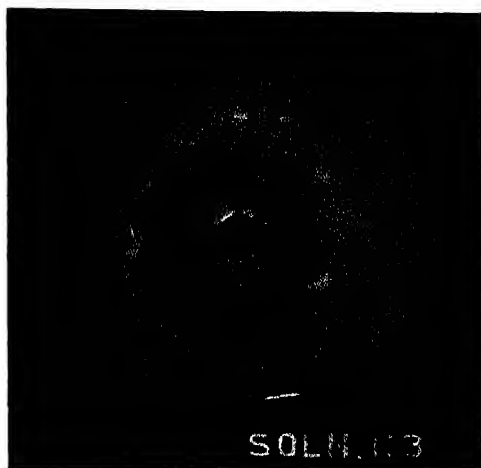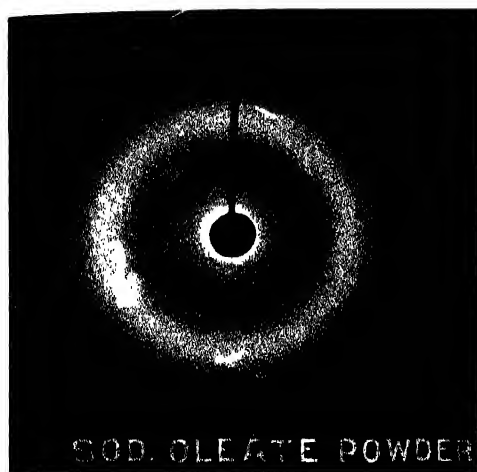
X-Ray Diffraction by Sodium Oleate Solutions

addition of traces of caustic alkali and by keeping them heated during the exposures.

It will be seen from the above description that the case of sodium oleate is quite distinct from those considered up till now, no other substance showing its characteristic ring at such a large dilution as $1:5$. The only obvious explanation for this consists in assuming the presence of particles of large dimensions consisting of several molecules, in the solution. This now becomes analogous to finely-divided gold suspensions which give rings in the same places as for the bigger crystals, found by Scherrer and others. The rings for sodium oleate solutions ($1:3$ and $1:5$) are of practically the same size as for the solid. This is similar to the phenomenon of swelling investigated by Katz, in which the water does not enter the lattice of the solute, *e.g.*, the swelling of sodium palmitate in 20% trichlorethylene and of chitin in water.

It will now be obvious why soap solutions behave like colloids and exert little osmotic pressure, the reason being that the sod. oleate molecules join together into a complex $(Na\ Ol)^x$ which behaves as a single big particle for exerting osmotic pressure. The gaseous scattering at small angles is due to simple molecules and ions which also exist in solution, while the general scattering is probably due to the OH' and Na' distributed at random in the solution. In the present experiments, scattering at very small angles is excluded by the lead disc used to cut out the central beam. But when the edge of the direct beam was just made visible, the scattering was found to be a maximum only at very small angles. This may be due to the 'ionic micelles' found by McBain from conductivity experiments.

On passing from $1:3$ to $1:5$ solution, the intensity of the sod. oleate ring diminishes, as also that of the gaseous scattering round the central spot. At the next dilution ($1:7$) the maximum due to sod. oleate is very weak, and has almost disappeared. The gaseous scattering near the centre is still dis-

tinctly visible, and there is a large amount of general scattering. At 1:9, there is still considerable scattering just below the water ring, though the gaseous scattering at the centre could not be distinguished from the intense general scattering inside the water halo. This shows that the micelles of undissociated sodium oleate do not appreciably break down into simpler units until after a dilution of 1:7. Even at 1:9 dilution or in a 10% solution micelles do exist, but they consist of a small number of simple molecules very much less than in the previous cases. It will also be seen from the results given in Table I, that the spacing corresponding to the outer edge of the gaseous scattering observed in solutions of concentrations down to 1:7, gives approximately the molecular dimensions of sodium oleate as calculated from its molecular weight and density. This can only be due to simple molecules of sodium oleate and to simple oleate ions existing in the solutions.

The presence of a definite ring in concentrated sodium oleate solutions shows that the molecules constituting the micelles are arranged side by side as in oleic acid or in any other long chain aliphatic compound. It is the presence of these micelles that is responsible for the abnormally low osmotic pressure and for the high viscosity of soap solutions. These observations are in entire agreement with those of McBain and his co-workers, and it is proposed to investigate the effects due to ionic micelles by using a narrower beam, and studying the effects very close to it.

Experimental.

The experimental arrangements were the same as those described in the previous communications from this laboratory. [18] The X-ray tube was worked by an oil-immersed transformer at about 50 K.V. A rotary converter supplied current to the primary at 160 V. The current in the primary was

18 Krishnamurti, Ind. Jour. Phys., iv, 498 (1928).

kept between 3-4 amperes and that in the secondary at 5-6 milliamperes.

A copper anticathode was used as in the previous cases, and the window out of which the X-rays emerged, consisted of very thin aluminium foil coated on the outside with rubber solution. Whenever slight leaks developed, they were traced to the window and effectually stopped by an additional layer of rubber solution.

A broad incident beam was used, which enabled the exposures to be cut down to about 2 hours, while at the same time all the details were brought out clearly. The central beam was cut out by suspending a lead disc in the path of the beam just near the photographic plate. The distance between the cell and the plate was 4·45 cms. The cell consisted simply of a gilded brass disc with a hole in the centre about 6 mm. in diameter and 1 mm. thick, which served to hold the liquid examined. Very thin mica was pasted on to both sides of the cell, after filling it with the solution to be examined. A few drops, about two or three, sufficed to fill the cell. The mica gave only the Laue spots, and did not interfere with the rings due to the liquids examined.

Dextrin.—Merck's extra pure dextrin, precipitated by alcohol, was used in these experiments. The requisite quantities of the substance and pure distilled water were weighed out, and the substance dissolved by slight warming. It was weighed again, and any loss of weight due to evaporation made up by addition of more water. The solutions were then filtered into a dry test-tube, the first portions of the filtrate being rejected. The filtrates were optically quite clear, a slight sediment which was present originally being removed by filtration. Only the most concentrated solution (2:1) which was very viscous was not filtered. This was kept heated to about 50°C during the exposure to prevent it from crystallising out. All the other solutions were examined at room-temperature (30°C).

Gelatin.—Specially purified ash-free gelatin of the Eastman Kodak Co., was used. This was supplied in thin sheets which were cut into small pieces to facilitate solution.

Two of these strips were pressed together into the cell for getting the solid pattern. The solutions were prepared by weighing out the constituents and warming till completely dissolved. The solutions except in the case of 1:1 solution were filtered, but they remained always opalescent in spite of repeated filtering. The concentrated solutions (1:1 and 1:2) were kept at about 50°C during the exposures to prevent them from setting into a jelly.

Sodium Oleate.—The substance was Kahlbaum's pure variety, which was washed with 95% alcohol and dried in an air oven at 110°C. The solutions were slightly opalescent, and hence traces of sodium hydroxide solution were added until they just cleared up. In addition, the solutions were kept heated to about 50°C during the exposures, and in the case of 1:3 solution, to about 65°C, since it was very viscous and showed a tendency to separate out on cooling. Hence, more concentrated solutions could not be examined. The exposures given in all the cases ranged from $2-2\frac{1}{2}$ hours. A blank taken with pure distilled water under the same conditions of exposure, did not show any appreciable excess of scattering near the central spot.

In order to get comparable results, the camera was adjusted in position, together with the lead disc cutting out the central beam, and was not disturbed during the whole series of exposures. The cell was taken out every time and replaced without altering the position of the camera. Lumiere plates were used throughout, and the conditions of development were kept similar as far as possible. The results are given in the following tables. The negatives were measured visually, and the spacings calculated according to the Bragg formula

$$a = \frac{\lambda}{2 \sin\frac{\theta}{2}},$$

λ having the value 1·54 for the Cu Ka radiation. Accurate measurements from the microphotometered records of the negatives will be published later.

TABLE II

Dextrin and Solutions.

Substance examined.	Inner Ring.				Outer Ring.			
	Inner margin.	Outer margin.	θ_1 in deg.	λ_1 in A.U.	Inner margin.	Outer margin.	θ_2 in deg.	λ_2 in A.U.
Powder.	15·1°	20·9°	18·1	4·91	...	...	...	...
2:1 Soln.	...	...	up to 9·6	9·24	16·3°	22·0°	19·2	4·62
1·1	...	...	up to 8·9	9·88	20·9	27·3	24·2	3·67
1:3	...	...	,,	,,	22·0	28·8	25·8	3·45
1·5	...	...	,,	,,	24·2	29·8	27·8	3·26
Water.	...	..	...	...	,,	,,	,,	,,

TABLE III A

Gelatin, Solid.

Rings	Inner margin.	Outer margin.	θ in deg·	λ in A.U.
(1)	5·2°	8·8°	6·4	18·80
(2)	17·5	28·7	20·9	4·24
(3)	...	...	31·0	2·88

TABLE III B.

Gelatin Solutions.

Solution	Corona.				Outer Ring.			
	Inner margin.	Outer margin.	θ in deg.	λ in A.U.	Inner margin.	Outer margin.	θ in deg.	λ in A.U.
1:1	...	...	up to 8·5	10·44	20·9°	28·8°	25·0	3·56
1:3	...	...	up to 5·8	15·31	28·4	29·8	27·3	3·26
1:5	...	...	,.	...	24·2	,,	,.	,,
1:10	...	:	very faint	...	,,	,.	.,	,,
Water.	...	...	...	...	,.	,,	,,	,,

TABLE IV

Sodium Oleate and *Solutions.*

Substance examined.	Corona.		Inner Ring.				Outer Ring.			
	Outer edge in deg.	Outer edge in A.U.	Inner margin.	Outer margin.	θ in deg.	λ in A.U.	Inner margin	Outer margin.	θ in deg.	λ in A.U.
Powder.	4·8	18·30	17·5°	21·5°	19·8	4·48	...	...	31·3	2·86
1:3 Soln.	11·1	7·94	17·8	21·5	19·8	4·48	25·3°	30·3°	27·8	3·20
1:5	,,	,,	17·5	20·9	19·8	4·48	24·2	30·3	27·8	3·20
1:7	,,	,,	Very feeble and diffused.				24·2	29·8	27·3	3·26
1:9	General Scattering.						,,	,,	,,	,.
Water.	...	...	...	...	...	...	,,	,,	,,	,,

It is proposed to study the diffraction effects in solutions of dyestuffs like congo red which are classed among semi-colloids, and also to study starch gels using a narrower beam,

so that the effects at smaller angles may be made visible. Some very interesting results have been obtained with the sol, gel and curd states of the same soap solution, some physico-chemical aspects of which have been studied recently.[19] The subject has been approached from the X-ray point of view, and the results will be published shortly.

This work has been made possible only by the generous assistance received from Prof. C. V. Raman, F.R.S., to whom my best thanks are due. I am also indebted to him for many valuable suggestions and helpful criticism during the course of this investigation.

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Laing and McBain, J. Chem. Soc., 117, 1506 (1920).

X-Ray Diffraction in Liquid Mixtures.

By

P. Krishnamurti.

(Plates XVII, XVIII and XIX.)

Abstract.

Several binary liquid mixtures have been investigated using the Kα radiation of copper. In all, about forty photographs were taken.

Aqueous systems.—Mixtures of various concentrations in which the other component was phenol, trimethyl carbinol, piperidine, pyridine, butyric acid, ethyl alcohol, glycerine and lactic acid respectively, were examined. In general, Wyckoff's conclusion that the pattern for the mixture is a superposition of those due to its components is not valid. A *very dilute solution* gives a pattern consisting of the water ring, and a general scattering inside the halo just as in dilute sugar solutions examined before. But in more concentrated solutions, the effects observed differ widely. With *phenol, trimethyl carbinol and piperidine*, the rings due to the two components exist separately in the pattern for the mixture, at approximately the same angles as in the pure liquids. The rings are, however, more diffuse than in the latter. Increasing amounts of water produce increasing intensity of the water ring. On the other hand, with *glycerine, ethyl alcohol and lactic acid* only one ring is observed, the water ring having contracted, and the ring due to the liquid having expanded. The addition of a small quantity of water to the pure liquid results in a widening of the ring for the latter, and makes its edges very diffuse. With further dilution, the maximum shifts to larger angles, and coincides with that of water in very dilute solutions. *Pyridine* solutions give patterns in

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which the pyridine ring has expanded slightly, but the water ring is in the same position. In a solution of *butyric acid* only one broad ring is found, due to a slight contraction of the water ring and a slight expansion of the butyric acid ring. Hence both these liquids form a transition between the two groups mentioned above.

An explanation is suggested that this difference between the two classes of solutions is due to the difference in the attractive forces existing between similar and dissimilar molecules in the mixtures. If the forces due to the former predominate, there is greater likelihood of similar molecules occurring together and *vice versa*. A distinction between the two classes is also indicated by other properties, notably miscibility and light-scattering power.

Non-aqueous systems.—A mixture of *methyl salicylate* and *o-nitrobenzaldehyde* gives a pattern almost identical with that obtained for either liquid. *Aniline and cyclohexane* mixtures above their critical solution temperature, give almost the same patterns as for the pure liquids. But with *cyclohexane and methyl salicylate*, where the two kinds of molecules are quite dissimilar, a different pattern is given for the mixture. The cyclohexane ring expands and considerable scattering is noticed both inside and outside the halo.

The presence of groups containing several molecules of each component separately, is postulated in aqueous solutions of the first group, by analogy with sodium oleate solutions previously considered. The solutions are probably of the same nature as Wo.Ostwald's ' Emulsion colloids,' the particles having however not very large dimensions.

1. *Introduction.*

The subject of X-ray diffraction in liquid mixtures was first attempted by Debierne, using the Debye-Scherrer method[1] and afterwards also by Wyckoff[2] who used the K_α radiation of molybdenum, and examined 1 : 1 mixtures of glycerine-water, carbon tetrachloride-benzene and carbon tetrachloride-methylene iodide. He concluded from the meagre data at his disposal that the pattern for the mixture was simply a

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[1] Debierne, Compt. Rend. 173, 140 (1921)

[2] Wyckoff, Am. Jour. Sci., 5, 455 (1923).

superposition of those of its constituents.   The experiments of Wyckoff, however, were quite inadequate as a basis for any conclusion, because his patterns showed insufficient resolution, the effects at small angles could not be observed and hence were ignored, and finally because he did not examine solutions of different concentrations.

In three previous communications,[1, 2, 3] the present author has studied the diffraction patterns obtained when a monochromatic beam of X-rays is passed through aqueous solutions of typical crystalloids, semi-colloids and colloids. It was found that dilute solutions gave in addition to the ring for water, a diffraction corona immediately surrounding the direction of the primary beam.   This corona was explained as due to the scattering of X-rays by the molecules of the solute distributed at random in the solution, and its extent was determined by the size of the dissolved molecule.   In more concentrated solutions, the arrangement of the molecules was no longer chaotic, and the corona gave place to a diffraction ring, the size of which increased with increasing concentration.   Slight deviations from this behaviour were noticed in the case of glucose and dextrin solutions, where the ring due to the water also began to contract in concentrated solutions.   An entirely different behaviour was met with in the case of sodium oleate solutions, which even in fairly dilute solutions (1 : 3 or 1 : 5) gave two distinct rings, one due to the water and the other to sodium oleate.   The formation of the latter ring was explained as due to the formation of micelles consisting of undissociated soap $(Na\ Ol)_x$ present in the solution, a conclusion in agreement with the views of McBain and his co-workers.   The extension of the study to binary liquid mixtures then naturally suggested itself.

[1] Krishnamurti, Ind. Jour. Phys., 2, iv, 501 (1928).

[2] Krishnamurti, Ind. Jour. Phys., 3, ii, 209 (1928).

[3] Krishnamurti, Ind. Jour. Phys., 3, iii, 307 (1928).

2. *The Mixtures Studied.*

Various types of binary liquid mixtures were studied in the investigation now described. They may be conveniently classified as follows :

(1) Aqueous Systems :—

(*a*) The second component is only partially miscible with water at ordinary temperatures, or if wholly miscible, separates on addition of sodium chloride.

(*b*) Liquids which are completely miscible and which cannot be thrown down by the addition of salt.

(2) Non-aqueous Systems :—

(*a*) The two components have molecules very similar in shape and size.

(*b*) Liquids that possess dissimilar molecules.

Water was chosen as one of the components, since it is a common solvent for many organic liquids, gives a pattern which is much larger than those given by the latter, and hence slight changes in any of the rings on dilution can be easily noticed. A few general remarks on the properties of liquid mixtures of various kinds will not be out of place here. It has been known for a long time that substances which are closely related chemically will show marked solvent action for one another, while those that differ considerably in constitution and chemical properties will be, as a rule, less soluble. An important advance in the study of liquid mixtures was made by Alexeeff,[1] who pointed out that several pairs of liquids partially miscible at ordinary temperature become infinitely miscible at some higher temperature, which was termed the 'critical solution temperature' by Orme Masson.[2] Somewhat later, it was discovered by Rothmund[3] that some

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[1] Alexeeff. Wied. Ann., 28, 305 (1886).

[2] O. Masson, Nature, 43, 345 (1891).

[3] Rothmund, Z. phys. chem., 26, 433 (1898).

liquids, notably derivatives of ammonia, are only partially miscible with water at higher temperatures but completely miscible at a lower temperature. A third kind of mixture was found by Hudson[1] in the system nicotine-water, which showed partial miscibility only between two definite temperatures but complete miscibility at all other temperatures. Mixtures of the first kind are said to possess an upper consolute point, those of the second a lower consolute point, while those of the third possess both these points. It has been pointed out by Crismer that the critical solution temperature of a pair of liquids is very much altered by the addition of a third substance, and Timmermans[2] has shown that the critical solution temperature is raised by the addition of a substance which is soluble only in one of the liquids, but is lowered when the substance dissolves in both liquids.

A very convenient basis for classifying liquid mixtures when one of the components is water, is furnished by their behaviour on addition of small quantities of sodium chloride. The 'salting out' of soap by addition of common salt to a concentrated soap solution is an example of the kind of effect to be expected. When several mixtures were thus investigated, it was found that they could be broadly divided into two groups, *viz.*, those that could be thrown down from their solutions by the addition of various amounts of sodium chloride, and those that cannot be separated into two layers by the same means. To the former class belonged mixtures of water with phenol, butyric acid, trimethyl carbinol, piperidine and pyridine respectively, while glycerine, ethyl alcohol and lactic acid solutions belonged to the latter. Among the liquids of the first type, it was also found that in the cases of butyric acid, phenol and trimethyl carbinol solutions, the critical solution temperature was raised by successive additions

[1] Hudson, Z. phys. chem., 47, 114 (1903).
[2] Timmermans, Z. phys. chem., 58, 129 (1907).

of salt, while in pyridine and piperidine the reverse was the case. This is probably connected with the evolution of heat on mixing the last two liquids with water; for, according to the law of Le Chatelier and Braun, the solubility will be increased by lowering the temperature, and naturally more salt would then be required to throw it out of solution. Thus it seems as if in the case of liquid mixtures showing an upper consolute point, the addition of salt raises it, whereas in the case of those having a lower one, it is lowered by the addition of sodium chloride.

Whether by a raising or lowering of the critical solution temperature, in the case of liquids of the first type, it is possible to get two layers at ordinary temperatures on the addition of suitable amounts of sodium chloride to their aqueous solutions. On the other hand, no amount of salt can throw down liquids of the second type from their aqueous solutions. Thus there seems to be a fundamental difference between the behaviour of these two types of solutions, which is probably connected with the fact that liquids of the latter type possess one or more hydroxyl or carboxyl groups, with a hydrocarbon chain which is fairly small. It is the object of the present X-ray investigation to find out the difference in the patterns of these two classes of solutions, and thus arrive at the probable arrangement of the molecules of each liquid in a liquid mixture.

3. *Results.*

(1) *Liquid mixtures—Aqueous systems.*—As a result of examining several solutions belonging to the first and second groups mentioned previously, it is found that there is a striking difference in the X-ray patterns of these two types. The
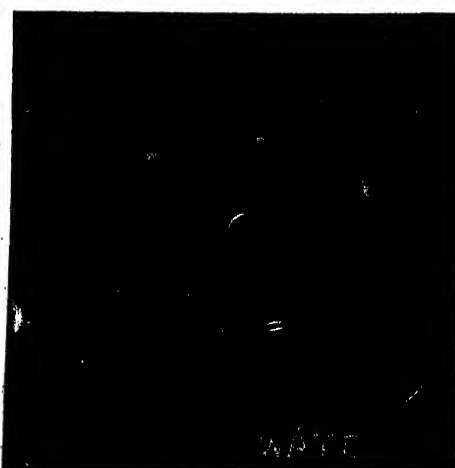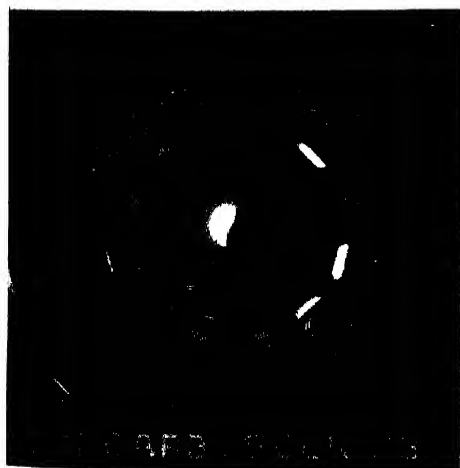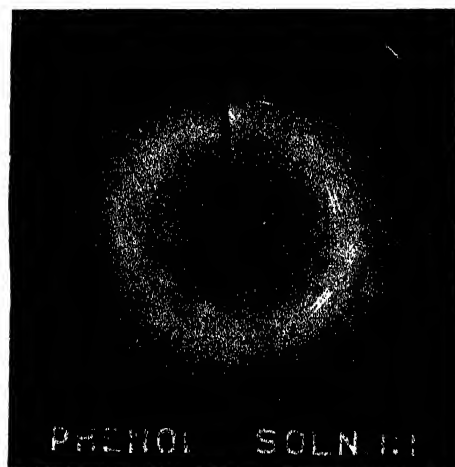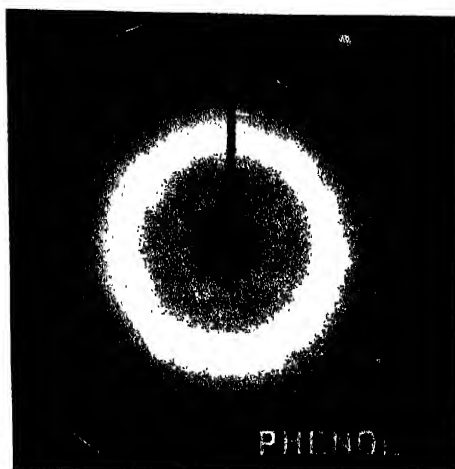
X=ray Diffraction in Liquid Mixtures

following classification is indicated as a result of these investigations :

I group. (Sodium oleate).	II group.
Phenol	Ethyl alcohol.
Trimethyl carbinol.	Glycerine.
Piperidine.	Lactic acid.

Transition group.

Pyridine.	Butyric acid.

It will be seen that this arrangement is essentially the same as the one arrived at by considering the effect of the addition of salt to their aqueous solutions. The diffraction patterns obtained with each liquid in the pure state as well as with its solutions at different concentrations will be described in detail.

The following liquids show similar patterns in their aqueous solutions :

Phenol.—The pure liquid gave two rings, the inner one being, however, faint. The addition of a very small quantity of water, simply made its pattern slightly more diffuse. The inner ring joined up with the centre, and gave only a faint, corona-like scattering. In a 1:1 solution, the phenol ring appeared in the same place, and the water ring which was larger was also visible though weaker and more diffuse than the phenol ring. There was some scattering between the water and phenol rings. In a 1:2 solution, the water ring had gathered up intensity, while the phenol ring remained in the same place. There was considerable scattering in the region between the two rings. In a 1:3 solution, the phenol ring was very weak and diffuse, while in 1:5 solution it could not be detected.

Trimethyl carbinol.—In this case also two rings were obtained for the pure liquid, the inner one being weaker. A 1 : 1 solution showed the ring due to the liquid and a very weak one for the water. The liquid ring was very slightly smaller than in the pure liquid. The small inner ring which appeared in the latter, had now joined up with the centre as in the case of phenol. In a 1 : 2 solution, the water ring had gained intensity, but the two rings were diffuse, and the region between the two not clear. The changes in general were very similar to those of phenol solutions.

Piperidine.—The pure liquid gave an intense ring with a very faint inner one. A 1 : 2 solution gave the water ring and the ring due to the piperidine in almost the same positions. The latter was stronger, and the region between the two fairly clear.

The next two liquids considered form a transition to the other group of liquids whose aqueous solutions give only one ring.

Pyridine.—The liquid pattern consisted of one sharp ring slightly bigger than that for piperidine. A 1 : 2 solution showed that the pyridine ring had slightly expanded. The water ring was in approximately the same position, and appeared as a continuation of the pyridine ring. The latter was stronger than that due to water.

Butyric acid.—The pure liquid gave rise to two rings, the inner one being slightly weaker than the outer. A 1 : 1 solution showed a broad pattern, the inner edge having about the same position as in the pure liquid, but more diffuse. The corona surrounding the central spot was very prominent. A 1 : 2 solution showed the maximum at a larger angle, the pattern consisting as before of a broad ring diffuse at the edges.

The following liquids belonging to the second group showed only one maximum :

Ethyl alcohol.—The pure liquid gave two rings of about the same intensity. In a 3 : 1 solution, the pattern was more

PIPERIDINE

PIPERIDINE, SOLN. 1:2

PYRIDINE

PYRIDINE, SOLN. 1:2

BUTYRIC ACID

BUT. ACID, SOLN. 1:1

X-ray Diffraction in Liquid Mixtures
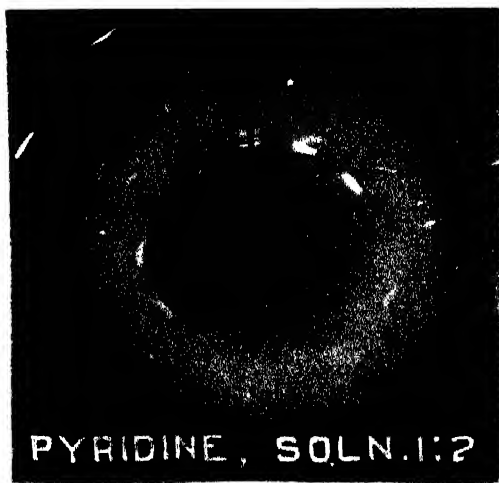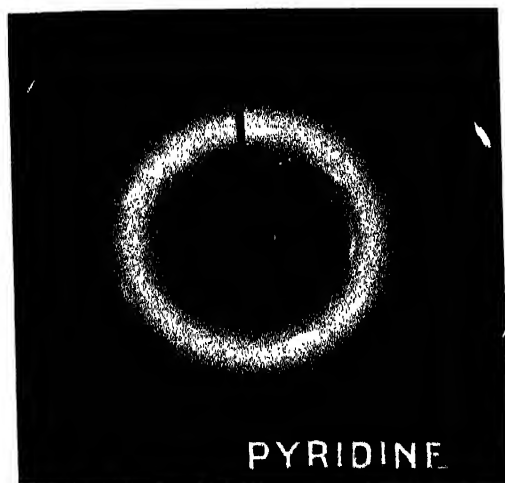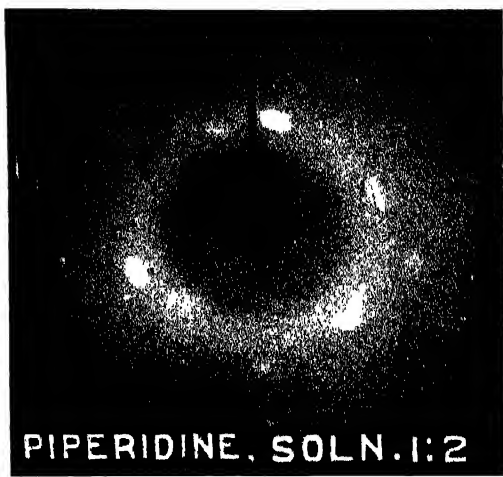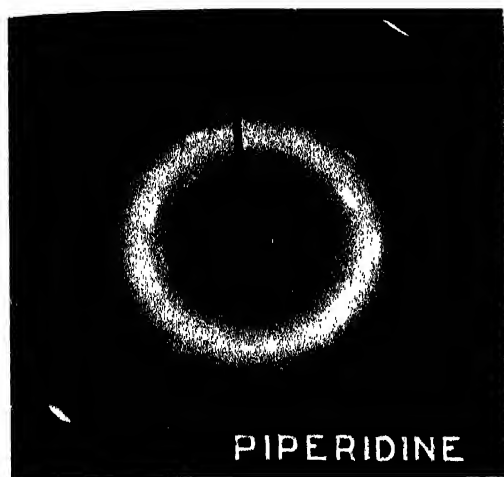
diffuse, and the inner ring had joined up with the centre. In a 2:1 solution, the ring began to expand, and this continued in 1 : 1 and 1 : 2 solutions. The rings were broad and diffuse at the edges. But in all cases, the inner edge of the alcohol ring expanded, and the outer edge of the water ring contracted, depending on the dilution. The inner corona was present in all patterns, though it decreased in extent and in intensity with dilution.

Glycerine.—The pure liquid gave a sharp ring, and the inner ring was very feeble. The patterns for the solutions showed the same changes as in ethyl alcohol, the position of maximum intensity occurring at an angle intermediate between those of its components, depending on the concentration. The inner scattering was weak, but still present in all the solutions.

Lactic acid.—Merck's extra pure specimen (sp. gr. 1·16) was used. It gave a ring with considerable internal scattering, but no inner maximum was present. The changes in the pattern on dilution were similar to the above two cases, though in this case, there was considerable inner and outer scattering in the patterns for the solutions.

It will be seen from the above description that the essential feature of the first group of liquids on mixing with water, is the formation of two distinct rings one due to the liquid and the other due to the water, with a more or less clear separation between the two. The features of the second group are entirely different, only one broad ring being produced in all cases, the position of maximum intensity varying between those of its components. There are also intermediate types, pyridine showing a greater similarity to those of group I, and butyric acid to those of group II.

There is, however, one feature common to all liquids. If the pattern for the pure liquid shows the inner ring, then a concentrated solution shows the corona at small angles, its intensity depending on that in the pure liquid, *e.g.*, trimethyl

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carbinol, butyric acid and ethyl alcohol solutions. A strong scattering inside the ring is present in all the dilute solutions.

(2) *Liquid mixtures—Non-aqueous Systems.*—(a) The first case where the two liquids are very similar in size and position of the substituent groups will be considered. Methyl salicylate and o-nitro benzaldehyde, both ortho disubstituted compounds containing groups of about the same size gave two rings each, of almost identical size. A 1 : 1 mixture was examined, and it was found that the pattern for the mixture was identical with that for either of the components. The two rings were quite clearly separated, and no other change in the pattern was observed. The system cyclohexane-aniline was next examined just above its critical solution temperature. No change in the outer ring was observed, but there appeared a faint corona-like scattering at small angles in place of the faint inner ring present in the pattern for pure aniline.

(b) When the two liquids differed widely in shape, size and polarity, and gave rise to different kinds of X-ray patterns in the pure state, the pattern for the mixture was greatly altered. Methyl salicylate gave two sharp rings, while cyclohexane gave an intense ring of intermediate size in the pure state. But a 1 : 1 solution showed a ring slightly bigger than the cyclohexane ring, but broader and more diffuse at the edges. There was also an intense scattering within the halo, and some without it, which might have been produced by the more unsymmetrical methyl salicylate. It showed clearly that the pattern for the mixture in this case, was anything but a superposition effect.

4. *Discussion of Results.*

It will be evident from the general statement of results given above, that we have to distinguish between two main groups of solutions, the members of each group giving similar

GLYCERINE

ETHYL ALCOHOL

GLYCERINE SOLN. 1:1

ET. ALC. SOLN. 1:1

GLYCERINE SOLN. 1:3

ET. ALC. SOLN. 1:3
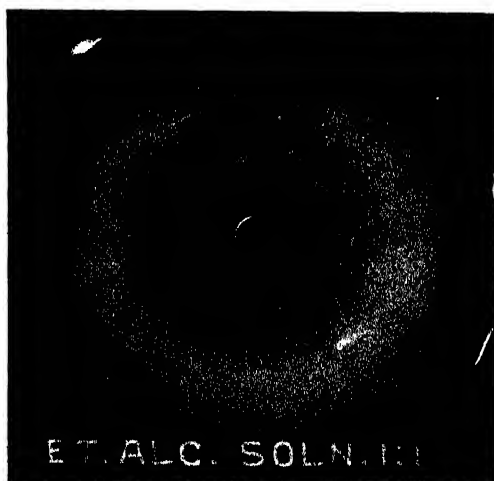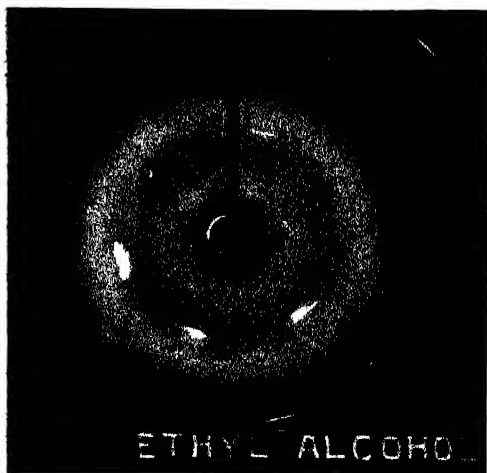
X-ray Diffraction in Liquid Mixtures

X-ray patterns and differing from those of the other. When a small quantity of one substance is dissolved in another, it is natural to expect from the analogy with sugar solutions,[1] that the smaller constituent is distributed at random in the other. This will be true only for *small* quantities of either substance; and once the proportion increases to some extent, this can no longer be the case, and the pattern should depend *prima facie* on the mutual arrangement of the molecules in the solution. The simplest case is one in which the two kinds of molecules are similar in size, shape and polarity, in which case the patterns for the pure liquids will also be similar, and so also the patterns for their mixtures. The substitution of one molecule for another hence makes no difference on account of their similarity. But if the two liquids differ to any slight extent in size or shape or polarity, and more especially if they give rise to different patterns in the pure state, the pattern for the mixture will depend on (1) the arrangement of similar molecules, (2) the arrangement of dissimilar molecules. Considering two molecular species A and B, the arrangement may consist of either

A A A A, B B B B
or
A B A B, B A B A

or both, depending on the mutual attraction between similar and dissimilar molecules.

The kinetic theory affords a basis for estimating these attractive forces. Van der Waals has shown that in the case of a binary liquid mixture containing $(1-x)$ gram-molecules of the first and x gram-molecules of the second component, the equation of state

$$\left(p+\frac{a}{v^2} \right) (v-b)=\text{R.T.}$$

Krishnamurti, *loc. cit*

is modified by substituting for the constants a and b, the following expressions :[1]

$$a = (1-x)^2 a_1 + 2x(1-x)a_{12} + x^2 a_2,$$

$$b = (1-x)^2 b_1 + 2x(1-x)b_{12} + x^2 b_2.$$

where a_1 and a_2 are the constants of molecular attraction for the first and second components, and a_{12} the constant of mutual attraction between the two. b_1 and b_2 are identical with Van der Waals b for the first and second liquid respectively, and is equal to four times the volume of a gram-molecule. b_{12} is derived from b_1 and b_2.

A consideration of the ' ψ surface ' or the free energy of the system defined with respect to x and v for any definite temperature, shows that for large values of v and when x approaches 1 or 0, positive values of $\frac{\partial^2 \psi}{\partial x^2}$ are obtained, which means that at a sufficiently large dilution, the two liquids will be completely miscible. The sign of the latter expression for given x and v will depend on the six coefficients, a_1, a_{12}, a_2, b_1, b_{12} and b_2, and these will decide whether the two liquids can mix with each other in all proportions. It is indicated that a large value of a_{12} will give large positive values to $\frac{\partial^2 \psi}{\partial x^2}$ and hence it will favour miscibility. On the other hand, large values of a_1 and a_2 will tend to decrease it and hence the tendency of the two liquids to separate will be greater. In other words, if the attraction between similar molecules is great, the two liquids will not be miscible, while a large attraction between dissimilar molecules will promote solution, a conclusion which is in general agreement with observed facts.

$\frac{\partial^2 \psi}{\partial x^2}$ can assume negative values mostly in the case of liquids which do not obey the law of corresponding states.

[1] Lorentz, Lectures in Theoretical Physics, Vol. II (Macmillan).

Here the surface has a longitudinal plait in the direction of v axis, showing the inability of the components to mix in all proportions. In fact, in a study of partially miscible liquids, it becomes apparent that in mixtures which show the critical solution temperature, one or both liquids are associated, and hence abnormal.

The next line of evidence which throws light on the state of molecular aggregation in liquid mixtures is from light-scattering data. In systems showing consolute temperatures, a very interesting phenomenon is observed just above the temperature at which the two layers separate. The liquid is transparent, but shows a bluish haze or critical opalescence, and the scattering is many times greater than in the pure liquids. This opalescence disappears on further heating, but the scattering is still of a high order of intensity. Smoluchowski[1] put forward the hypothesis that the optical effect is due to spontaneous local changes of concentration arising from molecular movement. Later, Einstein[2] derived a formula for the opalescence of a mixture from the variation of its refractive index and of the partial vapour pressures of its components with the change in concentration. This was found to hold good only near the critical solution temperature by Raman and Ramanathan,[3] who have shown that for obtaining the total scattering, three factors should be taken into consideration :

(1) Local fluctuations of concentration.
(2) Local fluctuations of density.
(3) Orientation of the molecules.

Since in all liquids the last two factors exist, if liquid mixtures show considerably more scattering, then it ought to be the effect of fluctuations of composition. The question then arises

[1] Smoluchowski, Ann. der. Phys., 25, 219 (1908).
[2] Einstein, Ann. der. Phys., 33, 1295 (1910).
[3] Raman and Ramanathan, Phil. Mag., 45, 213 (1923).

as to what actually happens in a liquid mixture when violent fluctuations of composition occur, *i.e.*, very near the critical solution temperature. If the mixture contains x gram-molecules of one component, then fluctuations mean that at any point in the mixture, the composition is not expressed by x, but by a higher or lower value, that of the other component also being lower or higher correspondingly. This can only happen if the attraction for similar molecules increases more than that for dissimilar molecules. The first effect of this attraction will be to bring together a few molecules each of A and a few of B together. But, later on, when nearing the critical solution temperature, A begins to attract more of its own kind, causing a deficiency of those molecules in some places. B also does likewise, and causes a deficiency of B molecules in some *other* places, and hence these fluctuations arise. Even if only a few molecules aggregate forming micelles of very small size, it will be sufficient to give a separate X-ray pattern. On the other hand, it requires a conglomeration of many more molecules to produce a corresponding abnormal effect in light-scattering. Hence X-rays begin to distinguish the heterogeneity of this solution much earlier than light does. It naturally follows that when light shows it, X-rays will show the same effects also, *i.e.*, it will produce no sudden change in the X-ray patterns at the critical solution point.

It will be seen that three distinct lines of evidence point to the existence of two different kinds of liquid mixtures, (1) from solubility relationships, (2) from kinetic theory, (3) from light scattering. From these points of view, the interpretation of the X-ray patterns for liquid mixtures becomes easier and the conclusions drawn fully justifiable.

The explanation for the superposition effects observed in aqueous solutions of group I mentioned previously, can be easily understood from a consideration of the case of sodium

oleate solutions discussed in a previous paper,[1] to which the changes in pattern of these solutions bear a close resemblance. It was pointed out that the separate ring in the pattern for the solution indicated the presence of micelles of undissociated sodium oleate (Na Ol) x, where x was a fairly large number. Similarly, we can postulate in the case of the above solutions, the presence of groups composed of several molecules of each component taken separately. If the two types of molecules be represented by A and B, the arrangement in the mixtures under consideration will be

$$A\ A \qquad A\ A \qquad A\ A$$
$$\text{and}$$
$$B\ B \qquad B\ B \qquad B\ B$$
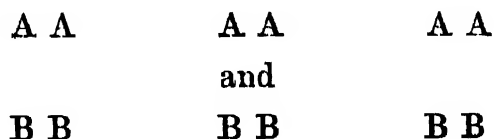
Two molecules of each are written close together to show the influence of association, *i.e.*, the arrangement of two polar molecules end to end, the polar groups being near each other. In such a grouping of molecules as shown above, if each group consists of a large number of molecules, then the molecular spacing will be practically the same as in the pure liquids. The intensities of the two rings will naturally depend on the relative amounts of the two species present, as well as on their scattering power. The inner ring present in any of the components will also be present in the pattern for the mixture; but since the spacing will not be so uniform as in the pure liquid, it will appear as a corona at small angles, its intensity depending on the dilution, and its extent on the size of the groups of molecules.

Passing next to liquids of group II, it will be seen that they are all associated, for, unless they are so, they will not be soluble to an unlimited degree in such a strongly associated liquid like water. In these cases, the affinity of the molecules of the same liquid to one another will be less

Krishnamurti, *loc. cit.*

than their affinity for water, and hence the possibility of the arrangement

$$AB \qquad AB \qquad AB$$

increases more and more. Supposing now that both A and B consist of double molecules, the above arrangement will happen only if the double molecules break up and unite with unlike molecules. In an aqueous system, the water molecules will be attracted to and collect round the polar group of the dissolved molecule. Two such water-liquid complexes will tend to attract each other, the optical centres of the solute molecules are brought closer together, with the result that the pattern begins to expand.

$$A.nB \qquad nB.A$$

will represent two such groups. B representing water molecules attach themselves to the solute molecules, the optical centres of two such groups are brought together still nearer, and the ring expands till it becomes identical with the water ring at a great dilution.

A consideration of the nature and extent of the corona surrounding the central spot is important, as we know from previous investigations that it is produced by random distribution of the molecules or micelles in the solution. The following table gives the extent of the scattering in some of the solutions where it is prominent. Col. (1) gives the spacing corresponding to the outer edge of the corona from the Bragg formula, col. (2) gives the average size of the molecule $\sqrt[3]{\frac{m}{d}}$. As the average size of the group indicated in col. (1) is $\sqrt[3]{\frac{n.m}{d}}$, we can easily calculate n, the number of simple molecules per group, which is given in col. (3).

The corona was evident in solutions of ethyl alcohol, butyric acid (1 : 1) and trimethyl carbinol (1 : 1). At larger

dilutions, it decreased in intensity when its presence and extent gave rise to some uncertainty, and hence were omitted. In these and in solutions of other liquids, a great deal of general scattering was noticed within the ring, which increased with dilution up to certain limits.

It should be pointed out that the values given for n are all very approximate, especially in the case of ethyl alcohol solutions, where alcohol-water complexes exist, but they are sufficient to show the order of magnitude of the groups present.

TABLE I.

Solution	(1) Extent of corona in A.U.	(2) $\sqrt[3]{\dfrac{m}{d}}$ in A.U.	(3) n.
Ethyl alcohol, 3 : 1	8·66	4·59	6·7
„ 2 : 1	9·00	„	7·5
Butyric acid 1 : 1	10·68	5·35	7·8
Trimethyl carbinol 1 : 1	13·80	5·37	17·0

The polarity and symmetry of the molecules are two factors which exert considerable influence on the diffraction patterns of solutions. A highly symmetrical substance like cyclohexane gives a very sharp ring, while a very unsymmetrical one like nitrobenzene gives a very diffuse halo. When the solubility and attraction relationships are equal in any two cases, this factor decides the nature and amount of scattering. Even in solutions, the sharpness or diffuseness of the ring due to liquids of group I is determined mainly by the symmetry of the molecule, piperidine giving a very

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sharp and intense halo in solutions, while trimethyl carbinol and phenol give more diffuse rings at the same concentration. In fact, polarity itself is intimately connected with the symmetry of the molecule, as when we compare the dielectric constants of the following liquids: mononitromethane (40), nitrobenzene (36), and tetranitromethane (2·1) or carbon tetrachloride (2·3) and chloroform (5·1).

The other factors which influence the nature and size of the halo are: (1) compound formation, (2) compressibility, (3) changes in volume on mixing. The first factor will be evident when substances of opposite polarity are mixed. The halo will then depend on the product of the reaction. But if this takes place to a limited extent, one can ignore its effects. The influence of the second factor in the case of pure liquids has been studied by Raman and Ramanathan.[1] The more compressible the solutions are, the more diffuse the haloes will be. The third factor influences the patterns since it affects the distance between neighbouring molecules. Ethyl alcohol, glycerine and to a less extent lactic acid, evolve heat on mixing with water, and evolution of heat is generally followed by a decrease in the total volume. Piperidine and pyridine also evolve heat on the addition of water. In this case the heat evolution might be due to the formation of small quantities of pyridinium and piperidinium hydroxides.

5. Some Analogies.

In the previous pages, some important conclusions have been arrived at regarding the aggregation of liquid molecules when dissolved in water. Two distinct classes of liquids were found, one of which is characterised by the great affinity for water, and the other in which the molecules of each liquid aggregate together and form groups containing several

[1] Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., 8, ii, 127 (1923).

molecules. The close similarity between solutions of the latter type and soap solutions was also pointed out. Soap solutions belong to the class of semi-colloids, or more strictly to 'colloidal electrolytes' of McBain. Hence it would be interesting to find out whether the liquid mixtures have any analogy with the behaviour of typical colloids, and in what way they differ from them, because this will lead to a better understanding of both kinds of solutions.

A colloid may be defined as a subdivision or dispersion of one kind of material in a second, with the degree of dispersion coarser than molecular, but not so coarse as to be detected by ordinary means. Of the two kinds of colloids, lyophobic and lyophilic, the former have no attraction for water, while the latter possess it to a great degree. Lyophilic colloidal solutions are viscous, gelatinising and not easily coagulated by salts, while the reverse is true about lyophobic ones. To the former class belong solutions of gelatin, soap and dextrin, while colloidal solutions of gold and silver belong to the latter.

We have to assume, as Wolfgang Ostwald has pointed out,[1] that a dispersion of liquid in a liquid forms the 'Emulsion colloid' or Emulsoid. These systems are not always lyophilic, liquid fat, for example, subdivided in water giving a lyophobic system. This is because the fat does not dissolve to any extent in the water ; on the other hand, soap does and hence forms a lyophilic system. "A lyophobic colloid results whenever the colloidally dispersed phase is not a solvent for the solvent ; a lyophilic colloid results when the dispersed material is such a solvent."[2] Hence, in a liquid—liquid system, one can find properties characteristic of either the lyophobic or lyophilic system, depending on the nature and mutual solubility of the two components.

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[1] Wo. Ostwald, Hand book of Colloid Chemistry (Tr. Fischer), 1919.
[2] M. H. Fischer, Mayo Foundation Lectures, 1925-26.

The essential similarity between these liquid systems and colloidal solutions is brought out clearly from the following properties, viz.,

(1) Coagulation by electrolytes.

(2) Frothing above the critical solution temperature, denoting a lowering of surface tension.

(3) Stability imparted by soap solutions.

The X-ray diffraction experiments indicate that liquids of group I, viz., phenol, trimethyl carbinol and piperidine in aqueous solutions give such 'Emulsion colloids,' since the molecules of each constituent are found to group together, forming micelles like the soap solutions.

(1) Sodium chloride is very effective in bringing about separation into two layers in the above solutions, different quantities being however required in the different cases.

(2) The system which shows a critical solution point, gives a froth just above that point, but not below it. This is similar to the case of soap solutions, and may be due to adsorption of the particles at the surface, followed by a lowering of the surface tension of the solution.

(3) It is a well-known fact that the addition of soap to a phenol-water mixture lowers its critical solution temperature, and makes it completely miscible at ordinary temperatures. Addition of salt again tends to separate it into two layers. Further, in the case of trimethyl carbinol, if it is precipitated from solution by the addition of salt, the addition of soap gets it again into solution. This seems very much akin to the case of protection of lyophobic colloidal systems by the addition of lyophilic ones like gelatin, soap, etc., which prevent the former from being coagulated by electrolytes (cf. the gold-number).

(4) Lastly, the enormous light scattering near the critical solution temperature, and even slightly above that temperature is similar to the Tyndall cone exhibited by solutions of colloids.

6. *Experimental.*

The experimental arrangements were the same as those used in the previous experiments, and described previously.[1] The X-ray tube with a copper anti cathode was worked by an oil-immersed transformer at about 50 K. V. The photographic method was employed, and the distance between the liquid and the plate was 4·45 cms. The direct beam was cut out by means of a lead disc suspended just before the photographic plate.

The cell for holding the liquid consisted of a brass disc 1 mm. thick, heavily gilded, with a hole in the centre, 6 mm. diameter. Two fine holes were drilled into the plate at an angle of about 30⁰ and after pasting very thin mica to the two sides of the brass plate, the liquid was introduced into the cell by means of these fine holes.

The exposures varied from 2-3 hours, with a current of about 4-5 milliamperes in the secondary. Lumiere extra rapid plates were used throughout, and the plates developed under identical conditions. A blank plate taken under identical conditions showed a small scattering confined to very small angles, and hence unless the scattering was very strong, it was not taken into account in the measurements.

The solutions were prepared by weighing out the requisite quantities of the two liquids, and after mixing thoroughly, introducing it into the cell, after rinsing it out with the same liquid. Freshly distilled water was used for preparing the solutions. Merck's or Kahlbaum's pure and extra pure specimens were used throughout. Glycerine was Merck's E. P. variety, sp. gr. 1·26, and lactic acid, of sp. gr. 1·16. Only in the case of ethyl alcohol solutions, the proportions are by volume. In all other cases, the proportions refer to weights of liquid and water respectively.

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[1] Krishnamurti, *loc. cit.*

The negatives were all measured visually, and the results are set forth in the following tables.

TABLE II.

Ethyl alcohol and Solutions.

Liquid	Inner Ring				Outer ring.			
	Inner margin	Outer margin	θ_1 in deg.	X_1 in A.U.	Inner margin	Outer margin	θ_2 in deg.	λ_2 in A,U.
Ethyl Alcohol	7·1°	11·4°	9·6	9·24	18·9°	23·1°	21·2	4·19
3:1	...	...	up to 10·2	8·66	18·9	23·7	21·7	4·08
2:1	...	...	up to 9·9	9·00	20·1	25·0	22·6	3·94
1:1	...	...	,,	.,	20·3	26·3	23·4	3·80
1:2	...	...	,,	,,	21·5	27·8	24·7	3·60
Water	...	...	...	...	24·2	29·8	27·3	3·26

TABLE III.

Glycerine and Solutions.

Liquid.	Inner margin	Outer margin	θ in deg.	λ in A. U.
Glycerine (1)	...	...	10·8	8·18
(2)	17·8°	21·5°	19·8	4·48
2:1	17·8	23·7	21·5	4·13
1:1	19·2	26·8	23·7	3·75
1:2	21·5	28·3	25·3	3·52
1:3	22·6	29·3	25·8	3·42
Water	24·2	29·8	27·3	3·26

TABLE IV.

Lactic acid and Solutions.

Liquid	Inner margin	Outer margin	θ in deg.	λ in A. U.
Lactic Acid	16·3°	22·0°	19·2	4.62
1 : 1	20·9	28·8	25·3	3·52
1 : 2	22·9	29·3	26·8	3·32
Water	24·2	29·8	27·3	3·26

TABLE V.

Butyric acid and Solutions.

	Inner Ring				Outer Ring.			
Liquid	Inner margin	Outer margin	θ_1 in deg.	λ_1 in A.U.	Inner margin	Outer margin	θ_2 in deg.	λ_2 in A,U.
Butyric Acid	5·8°	10·2°	8·6	10·22	16·9°	21·5°	19·2	4·62
1 : 1	...	...	up to 8·3	10·63	16·9	25·3	22·0	4·03
1 : 2	...	...	...	...	18·1	28·8	24·7	3·60

TABLE VI.

Trimethyl carbinol and Solutions.

Trimethyl Carbinol	6·7	10·2	8·6	10·22	16·0	19·5	18·1	4·91
1 : 1	...	...	up to 6·4	13·80	15·7	18·6	17·5	5·07 ⎫
							27·3	3·26 ⎬
1 : 2	...	...	...	...	14·5	19·2	17·5	5·07 ⎫
					23·7	29·8	27·3	3·26 ⎬
Water	...	...	...	...	24·2	29·8	27·3	3·26

TABLE VII.

Phenol and Solutions.

Liquid	Inner margin	Outer margin	θ in deg.	λ in A. U.
Phenol	6·7°	9·6°	8·0	11·20 ⎱
	16·3	20·3	18·3	4·83 ⎰
2·5 : 1	15·7	19·8	18·1	4·91
1 : 1	15·7	19·8	18·1	4·91 ⎱
	25·3	28·8	27·3	3·26 ⎰
1 : 2	16·3	20·3	18·1	4·91 ⎱
	25·3	28·8	27·3	3·26 ⎰
Water	24·2	29·8	27·3	3·26

TABLE VIII.

Piperidine and Solution.

Liquid	Inner margin	Outer margin	θ in deg,	λ in A, U.
Piperidine	...	...	7·1	12·52 ⎱
	16·0	19·5	18·1	4·91 ⎰
1 : 2	15·7	19·2	17·7	5·00 ⎱
	24·7	28·8	27·3	3·26 ⎰

TABLE IX.

Pyridine and Solution.

Pyridine	16·9	20·3	18·9	4·68
1 : 2	19·8	28·8	22·3	3·98
Water	24·2	29·8	27·3	3·26

TABLE X.

Methyl Salicylate—Cyclohexane.

Methyl Salicylate	11·2	15·4	13·3	6·65
	20·9	27·2	23·5	3·78
Cyclohexane	15·1	19·2	17·5	5·07
1 : 1 mixture	15·7	20·3	18·1	4·91

A more detailed examination of liquid mixtures with reference to any changes that might occur just at the critical solution temperature, especially at small angles to the primary beam is being carried out. The preliminary experiments in which butyric acid solutions were examined at the critical solution point (raised to the ordinary temperature by addition of about 1·5% of NaCl to a 1:2 mixture), show that no very great changes could be expected.

The above investigations were carried out in the chemical laboratories of the Indian Association for the Cultivation of Science. This work has been made possible only by the inspiration and guidance of Prof. C. V. Raman, F. R. S., to whom the author's best thanks are due.

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7

A Classical Derivation of the Compton Effect

BY

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ABSTRACT

With the aid of an atomic model in which the electrons are regarded as a gas distributed in a spherical enclosure surrounding the nucleus, it is shown that the classical wave-principles lead directly to a quantitative theory of the Compton effect and an explanation of the known experimental facts in connection with it.

1. *Introduction.*

As the simplest possible model of a spherically symmetrical atom, consider a spherical enclosure of radius R within which are imprisoned a certain number Z of electrons. We shall assume that the electrons move about within the enclosure like the molecules of a gas. They are subject to the influence of a central field of force, but are prevented from coalescing with it by the energy of their movements and their mutual repulsions. Our atom model is placed in the path of a plane train of waves of definite frequency. What would be the nature of the secondary radiation emitted by the atom? We shall proceed to discuss this problem on the classical wave-principles.

It will be assumed that each of the electrons is periodically accelerated along the direction of the electric force in the incident waves and emits secondary waves whose amplitude at a distance r is given by the expression $- e^2 \sin\theta/mc^2 r$,

where e, m and c have the usual meaning, and θ is the angle between r and the electric force in the incident waves. The problem of determining the secondary radiation at a distance from the atom resolves itself into that of finding the sum of Z vibrations of equal amplitude but whose phases are different. An important point is that as the electrons have been assumed to be mobile, the phase-relations between the Z vibrations are continually variable with time. Has the problem of finding the resultant of Z such vibrations any definite meaning or answer?

2. *Theory of Random Interferences.*

The question raised in the foregoing paragraph is very similar to those which continually arise in such optical problems as the theory of coronas, the scattering of light by the molecules of a fluid and the like. We shall consider the mathematical formulation of our problem a little later, but the answer to it can be given forthwith by analogy with the known results in the optical cases referred to. The resultant of the Z vibrations can be divided into two parts. *The first part* is entirely determinate, its amplitude being a function of the angle between the primary and secondary rays which is *invariable* with time, its frequency is the same as that of the incident radiation, and its phase is definitely connected with it for each given direction. The *second part* is entirely *indeterminate*, so that neither the amplitude nor the phase can be specified at any given time or in any given direction, and consequently the frequency is also variable. Nevertheless, it is possible to specify the *statistical expectation of intensity* of this second and highly fluctuating type of secondary radiation, that is to say, the average value to which it tends in the mean of a large number of trials, and to determine the manner in which it tends to be distributed with reference to direction. This possibility of subdividing the resultant into

two parts, one of which is stationary and determinate, and the other is fluctuating and indeterminate except in a statistical sense, follows in a strictly mathematical way from the theory of random interferences.

3. *Analysis of Secondary Radiation.*

We may now proceed to demonstrate the foregoing statements.

To enable the secondary radiation to be evaluated in a simple manner, we shall assume that the electrons move independently of each other in the spherical enclosure within which they are confined, and that the probability of any specified electron being found within a volume element dV of the enclosure is $\chi(\rho)\, dV$, where $\chi(\rho)$ is a known function of the distance ρ of the volume element from the centre of the sphere. As the probability of the electron being found within the enclosure is unity, $\chi(\rho)$ must satisfy the condition

$$\int_{0}^{R} 4\pi\rho^2\chi(\rho)d\rho = 1 \qquad \dots \ (1)$$

The sum of the Z vibrations at some distant point in some specified direction making an angle 2ϕ with the incident rays is

$$-\frac{e^2 \sin\theta}{m\,c^2\,r}\Big[\cos(2\pi vt+\chi_1)+\cos(2\pi vt+\chi_2)+\dots+\cos(2\pi vt+\chi_z)\Big]\dots \ (2)$$

where $\chi_1, \chi_2, \dots\dots\chi_z$ are the phases of the vibrations to be added. The resultant intensity is

$$\Big[=\frac{e^4\ \sin^2\theta}{m^2\ c^4\ r^2}\Big[Z+2\textstyle\sum\cos(\chi_1-\chi_2)\Big] \qquad \dots \ (3)$$

where the summation within the brackets extends over the $\frac{1}{2}Z(Z-1)$ terms of the form cos $(\chi_1-\chi_2)$. The phase differences $(\chi_1-\chi_2)$ etc., may be expressed in terms of the positions of the two electrons concerned in each case. These positions are sufficiently specified by the co-ordinates $\mu_1, \mu_2,\ldots\rho_1, \rho_2,\ldots$ where ρ is the radial distance of the electron from the centre of the sphere and μ is the direction-cosine of ρ with respect to the bisector of the angle between the incident and scattered rays. The statistical expectation of the value of cos $(\chi_1-\chi_2)$ in a large number of trials is given by the real part of the quadruple integral

$$4\pi^2 \int_0^R \int_0^R \int_{-1}^{+1} \int_{-1}^{+1} e^{i\psi\mu_1} e^{-i\psi\mu_2} \chi(\rho_1)\, \chi(\rho_2)\, \rho_1^2 \rho_2^2 d\rho_1 d\rho_2 d\mu_1 d\mu_2 \ldots \quad (4)$$

where $\qquad\qquad\qquad \psi = 4\pi\rho \sin \phi/\lambda.$

Since the variables ρ and μ are all independent, the integration with respect to μ_1 and μ_2 is readily effected. The quadruple integral(4) thus reduces to

$$\left[\int_0^R 4\pi\rho^2 \chi(\rho)\, \frac{\sin \psi}{\psi}\, d\rho \right] \qquad\qquad \ldots \quad (5)$$

We shall write (5) in the form F^2, where F is evidently a function of R, λ and the angle ϕ. Multiplying F^2 by $\frac{1}{2}Z(Z-1)$ and substituting in (3), the latter reduces to the extremely simple form

$$I = \frac{e^4 \sin^2 \theta}{m^2 c^4 r^2} [Z^2 F^2 + Z(1-F^2)] \qquad\qquad \ldots \quad (6)$$

Equation (6) may be written in the form

$$I = I_1 + I_2, \quad \text{where}$$

$$I_1 = \frac{e^4 \sin^2 \theta}{m^2 c^4 r^2} Z^2 F^2 \tag{7}$$

$$I_2 = \frac{e^4 \sin^2 \theta}{m^2 c^4 r^2} Z(1 - F^2) \quad \dots \quad (8)$$

The two parts I_1 and I_2 of the secondary radiation are fundamentally different in their physical nature as already remarked in the preceding section.

4. *The Two Types of Secondary Radiation.*

We may point out that the first of the two types of secondary radiation into which we have resolved the emission from the atom is obviously the *diffracted radiation* from the atom. This is clear from its proportionality to Z^2, and from the form of the function appearing in (5). The clearest proof of its nature is however given when we attempt to find by the methods of the electromagnetic theory of light, the intensity of the diffraction-pattern due to a dielectric sphere. If the dielectric constant of the material of the sphere is a function of the radial distance from the centre and is given by the relation $K - 1 = \chi(\rho)$ where $\chi(\rho)$ is assumed small compared with unity, the intensity of the diffracted radiation is given by the expression

$$\frac{\pi^2 \sin^2 \theta}{r^2 \lambda^4} \left[\int_0^R 4\pi \rho^2 \chi(\rho) \frac{\sin \psi}{\psi} d\rho \right]^2.$$

The identity of form of this integral with that appearing in (5) and (7) makes the nature of the latter evident.

Thus, of the two terms appearing in (6), the first term namely (7) is a perfectly determinate and invariable part which is the diffraction pattern of the atom. Hence, it

follows that the second term in (6), namely (8) represents the *statistical expectation of intensity* of a quantity whose value in individual trials is indeterminate. This is clear from the fact that this term arises from a summation of amplitudes with entirely indeterminate phase-relationships which consequently can give no definite result in any individual trial. The proportionality to Z instead of to Z^2 is significant in this connection. A summation of the intensities instead of the amplitudes of the effects of the electrons is permissible for the determination of a statistical average only when the effects under consideration are *completely uncorrelated* in phase. An important point to be noticed also from equation (1) and expression (5) is that when $\phi = 0$, that is, in the direction of the primary beam, $F^2 = 1$ and hence the expression (8) vanishes. This could have been expected *a priori*, for in the forward direction, the Z vibrations to be added have completely determinate phases, and hence the indeterminate part of the sum of the Z vibrations must vanish.

The first type of secondary radiation being the diffraction by the atom, what meaning should we attach to the second and highly fluctuating type of radiation which is indicated by our atom-model? In this connection, we may remark that the possibility, or rather, the necessity for separating the secondary radiation into two distinct parts arises only when we employ a dynamic atomic model. In static atomic models where the electrons are supposed to occupy fixed positions within the atom, the phase-relations between them have always fixed values for any fixed direction, and the entire effect produced by the electrons is single and indivisible; we would have merely a diffraction-pattern or "structure-factor" for the entire atom, differing considerably no doubt from that due to a smoothed-out distribution, but belonging to the same physical class of phenomenon. With static atom-models, therefore, it is not permissible to speak of any "independent" scattering by the electrons.

From the fact that the statistical expectation of intensity of our second type of radiation is proportional to Z, the atomic number, the reader might be tempted to suppose that this is simply the J. J. Thomson—C. G. Barkla type of scattering by the Z electrons in the atom acting "independently." *Such a view would be erroneous.* For, in the first place, our formula is not simply the Thomson expression but appears with a very significant multiplying factor $(1 - F^2)$. But a more vital and fundamental difference is that our expression represents merely the statistical average of a quantity that *fluctuates with time.* This is essentially the result of using a dynamic atomic model, and the fluctuating effect involves also corresponding fluctuations with the time of the state of the atom itself, an idea not contemplated in the Thomson—Barkla theory. In fact, our investigation discloses that the so-called "Thomson scattering by the Z electrons acting independently" has no real existence either in a static or a dynamic atomic model.

As remarked above, the fluctuations with time of the secondary radiation from the atom involve corresponding fluctuations in the electrical state of the atom which we may attribute to the movements of the electrons. If we postulate that the atom does not or cannot fluctuate, the fluctuating type of secondary radiation cannot exist. On the other hand, if we believe that our atom-model is not a wholly erroneous picture of the real atom and are prepared to concede the inference from it that a fluctuating type of secondary radiation from the atom does exist, then we must be equally prepared to accept the corollary that its emission is accompanied by a simultaneous fluctuation in the electrical state of the atom, the two phenomena in fact being inseparably linked with each other.

We shall now proceed to identify the second or fluctuating type of secondary radiation with the Compton Effect. It may seem surprising to be told that the classical wave-princi-

ples thus lead us directly to the existence of this effect and indeed also suffice to indicate its observed physical characters. The belief that the classical wave-principles are not easily reconcilable with the phenomena of the Compton Effect must be ascribed, however, not to any defect of the wave-principles, but to the fact that they have not been interpreted correctly in the past in relation to the present problem. The existence of at least two different types of secondary X-radiation, one of which is of a highly "fluctuating" or incoherent character is the cardinal experimental fact which requires explanation, and we have seen already that the classical wave-principles taken together with a dynamic atom-model lead us to it very naturally. We shall presently see that they also explain the other facts known experimentally about the Compton Effect.

Our identification of the classical fluctuating secondary radiation with the Compton Effect is not merely qualitative. It may be developed mathematically and proves itself to be solidly based.

5. *The Characters of the Compton Effect.*

From equations (7) and (8) written above, and from the nature of the function F^2 which involves R, λ and ϕ, it is readily seen that the ratio of the two types of secondary radiations depends on Z the atomic number, upon the ratio of the wave-length λ to the radius R of the atom, and upon the angle of diffraction 2ϕ. We shall consider these in order.

As already remarked, the fluctuating type of radiation vanishes when $\phi = 0$. With increasing angle of diffraction, the value of F^2 falls down from unity rather quickly, and ultimately reaches rather small values at large angles. The march of the function F^2 with ϕ depends of course on the structure-factor of the atom. The second type of radiation is, therefore, relatively to the first quite inconspicuous at small angles of diffraction. It reaches importance only when the

angle of diffraction is such that F^2 is a small fraction of unity, and then becomes quite comparable with the regularly diffracted radiation.

. The ratio of the second to the first type of radiation is largest for elements of low atomic number and becomes very small for elements of high atomic number. For elements of low atomic number, the two types of radiation are of comparable intensity even at very moderate angles of scattering ; at larger angles, the fluctuating radiation becomes much the more conspicuous of the two.

For any given angle of diffraction, F^2 becomes smaller with decreasing wave-length of the incident radiation. Hence the ratio of the fluctuating to the stationary type of radiation increases with increasing hardness of the incident X-radiation. The angle of diffraction 2ϕ at which the two become of comparable intensity becomes smaller at the same time, $\sin\phi$ being in fact proportional to λ.

We see therefore that the experimentally known facts regarding the ratio of the "unmodified" and "modified" types of X-ray scattering and its variation with the atomic number of the scattering element, the wave-length of the incident radiation, and the angle of diffraction are correctly indicated by the very simple theory developed in the foregoing pages.

Our model atom is, of course, rather crude in its constitution. Its most defective feature is the assumption of an artificial barrier preventing the electrons from escaping outside. Such an artificial barrier is not really needed. In reality, any of the electrons is free to wander away from the atom into space if its kinetic energy should exceed the potential energy of its position in the central field of force. On the other hand, if its kinetic energy be less than this value, it cannot leave the atom and no barrier is needed to prevent its escape. If we imagine an electron to be so feebly bound that a small increment of energy would liberate it, such addition of

energy would enable it to wander off from the atom. The escape of an electron from the atom may therefore be legitimately regarded as a possible mode of "fluctuation" in the electrical state of an atom, and one which is especially likely in the case of atoms in which the electrons are very loosely bound. We may therefore, without an undue stretch of language claim that considerations of a purely classical nature not only definitely predict the existence of a highly fluctuating type of secondary radiation from atoms, but also indicate that the fluctuation of the atom which must accompany the emission of such radiation consists of the ejection of an electron from it.

To be strictly logical, of course, we must be prepared to admit the possibility of other possible modes of fluctuation of the atom and the existence of corresponding special types of secondary radiation from it. Our simple atom-model with its virtually free electrons is not however capable of dealing with such cases quantitatively.

To avoid misapprehension, it should be made clear that the "fluctuations" of the atom we are considering are quite different in nature from the "fluctuations" contemplated in thermodynamics and kinetic theory. We are here concerned with the "fluctuations" of the atom from its normal condition under the influence of external radiation. Whether simultaneous thermal excitation would modify the results is a question into which we need not enter here.

6. *The Change of Wave-length.*

It now remains to consider the question of the change of wave-length and its relation to the motion of the ejected electron. Any type of secondary radiation from particles in motion necessarily. involves changes of wave-length. Since the fluctuating secondary radiation is associated with the motion of an electron from within to outside the atom, we may naturally expect its frequency to be altered by reason of the

Doppler effect. If we assume the electron to move with a velocity v in the direction of propagation of the primary waves, the wave-length of the spherical secondary waves emitted by it and observed in a direction making an angle χ with the primary waves is

$$\lambda' = \lambda + \lambda \frac{v}{c} (1 - \cos \chi) \tag{9}$$

Since we have assumed the electron to be periodically accelerated in the direction of the electric force, the only other possible way in which the incident radiation can act on the electron is by way of radiation pressure or electromagnetic momentum. This must be in the *forward* direction, for the secondary radiations from the electron being spherically symmetrical, they can have no resultant momentum in any direction. Thus, classical wave-principles justify (9) at least in form. We shall be doing no violence to them, though we may be offending Newtonian mechanics, by taking the forward momentum of the scattering electron to be the same as that of finite train of plane waves having the total energy $h\nu$. We then obtain

$$\lambda' = \lambda + \frac{n}{mc} (1 - \cos \chi) \tag{10}$$

which is the Compton equation derived on the classical wave-principles.

In obtaining (10), we have considered the *electron*, and altogether ignored the *atom* with which it is associated before expulsion. The radiation from the atom does not consist of simple spherical waves as contemplated above, but of the complex fluctuating disturbance given by equation (6) of which the second part represents only a "statistical expectation" of intensity. Hence, we should be very far from being justified in assuming without further examination that the

argument adduced above is valid for the case of the atom as distinguished from that of the free electron. Nevertheless there is good reason for accepting (10) as representing *statistically* the observed relation between wave-length and direction of observation, at least as an approximation. For, when the angle of diffraction is not too small, and especially for elements of low atomic number, equation (6) gives the statistical expectation of intensity as practically Z times that of a single free electron, and hence (10) may be regarded as *statistically* valid to a close approximation.

It is a different matter if we ask what are the possibilities in any *individual* trial. To find an answer to this, we have to consider more closely the character of the fluctuating disturbance radiated from the atom. We must remember that not only is its intensity variable with time, but also its angular distribution, so that apparently we have no method, *a priori*, of finding what it would be in any individual trial. A way out of this difficulty is however indicated by the well-known general solution of the equation of wave-propagation discovered by Whittaker (See "Modern Analysis." Camb. University Press); Whittaker's solution shows that even a most arbitrary type of wave-disturbance can be represented as the superposition of plane trains of waves travelling in all directions through space. We may thus analyse our fluctuating radiation into sets of plane waves travelling in different directions. Since the incident waves are themselves plane and periodic, we may accept the hint given by equation (10), and assume that it gives, as an approximation, the wavelength of the plane train travelling in the direction specified by the angle χ as the result of such analysis. In any *particular trial*, therefore, the fluctuating part of the radiation emitted by the atom may be conceived as consisting, approximately, of a single such plane wave train or a group of closely adjacent plane wave-trains. In finding the corresponding velocity and direction of motion of the ejected electron, we have to

take into account the momentum of the incident wave as well as that of the unsymmetrically scattered secondary wave. We understand in this way, why in any individual trial, the electron may be ejected in directions other than that of the primary ray. Its actual velocity and direction of motion depend on the incident and scattered waves jointly. Incidentally, it becomes evident why the argument of the "triangle of momenta" by which Compton obtained his formulæ gives the same result for the change of wave-length as the simple classical theory of the emission of spherical secondary waves by the electron.

X-Ray Diffraction in Liquids of the
Terpene Series

BY

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(Plate XX.)

ABSTRACT.

Employing Cu Kα radiation, a systematic study was made of the X-Ray haloes given by twenty-one liquids belonging to the terpene series. Five long chain olefinic terpenes; geraniol, linalol, rhodinol, citral and citronellal showed peaks at nearly the same angle, corresponding to a diameter of 4·95Å. In the first three, there was also a second faint halo at an angle smaller than the principal maximum. The next liquid terpineol, which is a derivative of a mono-cyclic terpene, had a diameter of 5·08Å, the inner halo in it being more prominent than with geraniol, linalol or rhodinol. The group of liquids menthone, carvone and thujone, with a CO group in the ring of the compound showed peaks corresponding to a diameter of 5·35Å. In the transition to the cyclic terpenes of the formula $C_{10}H_{16}$, there was a further increase in the diameter, the values obtained with these liquids being from 5·45Å to 6Å. Of these eight, five, namely; terpinene, *d.* limonene, *d* (*l*) limonene *d.* *a.* phellandrene and sylvestrene were monocyclic compounds, but only one, sylvestrene showed a second faint halo at smaller angles. Camphene, *d.* pinene and *l.* pinene are dicyclic. The halo for camphene is of special interest, being very sharp and without any trace of an inner ring. The pinenes give each of them two haloes. The four sesquiterpenes, cadinene, inene, caryophyllene and cedrene showed a remarkably diffuse halo between 15 and 25°, outside the principal one. The diameter corresponding to the strong halo was about 7Å in all of them.

The gradual increase in the diameter of the molecules of the liquids and the approximate constancy for each class is the most notable feature. The chart accompanying the picture shows the approximate positions and intensities of the peaks.

The fundamental idea that the X-Ray diffraction peaks in liquids occur at distances equal to the mean molecular distances, with the additional conception that the distribution of molecules around any molecule depends on their form and symmetry, seems to be sufficient for an explanation of the nature of the haloes. On the basis of these ideas, the expectation of a sharp halo in liquids with symmetrical molecules, is remarkably justified in the sharpness of the halo and the structural symmetry of camphene.

Introduction.

X-Ray diffraction in liquids has been a subject of considerable research, especially during recent years. Beginning from the observation of Debye,[1] X-Ray diffraction patterns of liquids have been experimentally studied by Debierne,[2] Keesom and Smedt,[3] Wyckoff,[4] Prins,[5] Sogani,[6] Stewart and others,[7] Katz and his co-workers[8] and Krishnamurti.[9] It will be sufficient here, to review some of the outstanding recent contributions in the field.

Sogani examined, in our laboratory, a number of liquids, such as the aliphatic hydrocarbons, higher members of the fatty acids, a few benzene derivatives and mercury. In the aliphatics and the higher members of the fatty acids, he found a constant size of the halo. In the case of benzene and its derivatives, the haloes differed considerably, depending on the group that was substituted. The halo for cyclohexane was

[1] Debye and Scherrer, Nachrichten Göttingen, 16, 16 (1926).

[2] Debierne, Compt. Rend., 173, 140 (1921).

[3] Keesom and Smedt, Proc. Roy. Soc. Amsterdam, 38, 116, 1922 and 86, 112 (1928).

[4] Wyckoff, Amer. Jour. Sc., 5, 460 (1923).

[5] Prins, Physica, 6, 315 (1926).

[6] Sogani, Ind. Jour. Phys. 1, 357, 1927; 2, 97, 1927; and 2, 377 (1928).

[7] Stewart and others, Phys. Rev. 30, 232, 1927; 31, 1, 1928 and 32, 153 (1928).

[8] Katz and co-workers, Zeit. fur. Phys., 45, 97, 1927; and 46, 392 (1928).

[9] Krishnamurti, Ind. Jour. Phys., 2, 355, 1928; 2, 495, 1928; and 2, 505 (1928).

found to be very sharp, when compared with those of other liquids and in mercury the ring was remarkably narrow.

In view of his observations, Sogani emphasised the importance of molecular form, arrangement and compressibility, on the dimensions, character and sharpness of the halo. The case of mercury is of special interest in this connection. It has a monatomic molecule and the lowest compressibility and the halo possesses features characteristic of these qualities.

About the same time, Stewart and his co-workers made a systematic examination of alcohols, acids and isomers of long chain compounds. In the case of alcohols and normal fatty acids, they invariably observed 2 haloes, the one at smaller angles being very faint relative to the outer. From the various observations on isomers of long chain hydrocarbons, alcohols, etc., they conclude that when a methyl or hydroxyl group is attached as a side branch to an alcohol chain, the diameter of the molecules increases by $0.6\overset{o}{A}$ and $0.4\overset{o}{A}$ respectively, whereas in a normal hydrocarbon chain a methyl group causes an increase of $1.04\overset{o}{A}$. In the case of the higher members of the aliphatic hydrocarbons, they also observe a constant angle for the diffraction peak.

Katz and his co-workers investigated a variety of compounds by the photographic method. The observations of Katz on polymerised substances, aldehydes and trisubstituted benzene derivatives are of great interest. Whereas polymerised substances, such as styrol, gave 2 haloes, only one was obtained in the non-polymerised state. Tri-methyl benzene, tri-methyl pyridine and most of the aldehydes showed the presence of 2 intense rings in the X-Ray patterns.

A systematic examination of benzene derivatives has been made by Krishnamurti. The ortho and meta di-substituted benzene derivatives invariably gave 2 haloes, whereas the para compounds, yielded only a single diffuse one. He also observed that the outer ring increased in brightness and definition, relative to the inner, as the sizes of the substituting

groups are increased. In another investigation, Krishnamurti examined a number of organic liquids, to find the extent of molecular association, from the nature and intensity of the faint inner haloes. From the fact that all liquids which he examined, showed the presence of a faint halo at small angles, he concluded that all of them were associated to different extents, for example ; benzene and ethyl alcohol gave a degree of association 1·4 and 3·6.

From the brief survey given above, it will be observed that each investigator had a different end in view and much yet remains to be done in the way of systematic investigation of a number of liquids belonging to one series. In the present case, therefore, attention is confined to the typical liquids belonging only to the terpene series, the object being to attempt a classification of the long chain, cyclic and sesquiterpenes by the method of X-Ray analysis, to examine the dependence of X-Ray diffraction patterns on the structure of molecules and in particular to obtain such information, as is possible, regarding the molecular form and dimensions, from these studies.

Experimental.

The source of X-Rays was a Shearer tube and the scattering wave-length was CuKα. The photographic method was employed.

Results.

The results of observations are embodied in the chart given below. The arrows indicate the angles corresponding to the different maxima. An idea of the widths of the peaks can also be had from the nature of the curves. The relative heights of the peaks for the same liquid indicate approximately, the relative intensities of the haloes. They have been reproduced by careful visual observations of the negatives.

			6° 16° 26
Long chain olefinic terpenes	1	Geraniol	
	2	Linalol	
	3	Rhodinol	
	4	Citral	
	5	Citronellal	
	6	Terpineol	
Cyclic terpenes with CO group	7	Menthone	
	8	Carvone	
	9	Thujone	
Mono and dicyclic hydrocarbon. terpenes	10	Terpinene	
	11	d. Limonene	
	12	d(l) Limonene	
	13	d. Phellandrene	
	14	Sylvestrene	
	15	Camphene	
	16	d. Pinene	
	17	l. Pinene	
Sesquiterpenes	18	Cadinene	
	19	Inene	
	20	Caryophyllene	
	21	Cedrene	

It will be observed from the chart, that the most striking feature is the gradual decrease of the angle of the diffraction peak, when we pass on from the long chain olefinic terpenes to the sesquiterpenes. For instance, beginning at 18°-4′, in the case of the long chain olefinic terpenes, the diffraction angle of the peak reaches a minimum of 12°-42′, in cedrene, which is a sesquiterpene of the formula of $C_{15}H_{24}$.

Each class has generally a constant diffraction angle for the principal peak, but varying within small limits. In the case of the mono- and di-cyclic terpenes of the formula $C_{10}H_{16}$, the limit of this variation is larger than in other classes of compounds. The reason for this will be evident, when we examine the structural changes of the isomers of this class.

Another prominent feature is that between one class and another, there is an interval for the angle of the diffraction peak. From the long chain olefinic terpenes to the ketonic derivatives of cyclic terpenes this interval is about 1·5°. Between the latter class and the next, i.e., the cyclic terpenes which are hydrocarbons of the formula $C_{10}H_{16}$, the difference of the angle of the peak is nearly half a degree. This is not so marked as between the other classes, nor is the structural change, as will be seen subsequently. During the transformation from the cyclic terpenes $C_{10}H_{16}$ to the sesquiterpenes, $C_{15}H_{24}$, the margin is very wide, being about 2 degrees.

Having set forth the general differences and progress of the haloes, we shall now make a brief mention of the special characteristics of each class and the liquids belonging to them.

In the olefinic long chain terpenes, the peaks of the principal haloes occur at nearly the same angle, 17·7° to 18°. In the first 3 liquids geraniol, linalol, and rhodinol, there are inner haloes, but in citral and citronellal (*vide* chart) these haloes have become extremely faint. On the other hand in the 2 latter liquids, the principal haloes are more diffuse than in the case of the former ones. Corresponding to the absence

of the faint haloes, this development is interesting. As will be seen later on, there are small structural changes too that have taken place in these cases.

Terpineol.—The peak for this liquid is at an angle of 17·4°. The inner halo is slightly more prominent and larger in size than in the case of open chain terpenes. From its chemical position between the former class and pinene, this liquid is of special interest to us and stands as a class by itself.

In the next step, we have the cyclic terpenes with a CO group in the ring. These are menthone, carvone and thujone. The angles of the diffraction peak for these liquids occur at 16·7° and are fairly constant. In menthone there is also a faint halo at 8·5°. The halo for carvone is diffuse, whereas for thujone it is much sharper.

When we pass on to the next series of liquids, which are cyclic-terpenes, $C_{10}H_{16}$, a further contraction takes place and the haloes now range between 16·1 and 15·3°. These liquids exhibit a variety and difference in the nature of their haloes, more prominent than in liquids belonging to the other classes, so far studied in the present case. Of the first five liquids in this class (10, 11, 12, 13, 14 in the chart) only sylvestrene has a faint inner halo. The principal haloes are of nearly the same diffuseness. The next liquid in the series, camphene, has a peculiarly sharp halo, as distinct from those of other liquids. Pinene shows 2 haloes, the inner one being nearly as prominent as the outer. These 2 extreme and typical cases are peculiarly interesting in showing the dependence of the X-Ray diffraction on the structure and symmetry of molecules.

In the last class of compounds, the sesquiterpenes ; the haloes are very remarkable in as much as they show 3 of them. The peaks of the principal haloes are at an angle of about 12·6° and vary within very small limits. Outside the principal halo, there is a diffuse one, beginning at an angle of 15° and extending to about 25° and the outer margins are

also diffuse. In cadinene, the outermost halo is fainter than in others, whereas in cedrene the inner one is absent. It is also a general characteristic of them to have a large amount of internal scattering, but the haloes can be clearly distinguished.

In the following table are given the intermolecular distances calculated according to the Bragg formula $a = \lambda / 2 \sin \frac{1}{2} \theta$. In the table, a_1 corresponds to the innermost peak, a_2 to the principal peak and a_3 to the outermost one. It may be remarked that in calculating a_3, the angle corresponding to the border of the diffuse halo is taken into account. The measurements of the peaks were made from the original negatives.

	Liquid.	a_1	a_2	a_3
1.	Geraniol	12·6	4·92	...
2.	Linalol	11·3	4·99	...
3.	Rhodinol	12·3	4·94	...
4.	Citral	...	4·91	...
5.	Citronellal	...	4·91	...
6.	Terpineol	10·9	5·08	...
7.	Menthone	...	5·83	...
8.	Carvone	...	5·36	...
9.	Thujone	...	5·36	...
10.	Terpinene	...	5·44	...
11.	d. Limonene	...	5·50	...
12.	d (l) Limonene	...	5·50	...
13.	d. a. Phellandrene	...	5·72	...
14.	Sylvestrene	10·9	5·81	...
15.	Camphene	...	5·75	...
16.	d. Pinene	10·1	6·02	...
17.	l. Pinene	10·1	6·02	...
18.	Cadinene	...	7·46	...
19.	Inene	...	7·00	3·6
20.	Caryophyllene	...	7·00	3·7
21.	Cedrene	...	6·96	3·7

Rhodinol — Thujene — Phellandrene — Camphene — Pinene
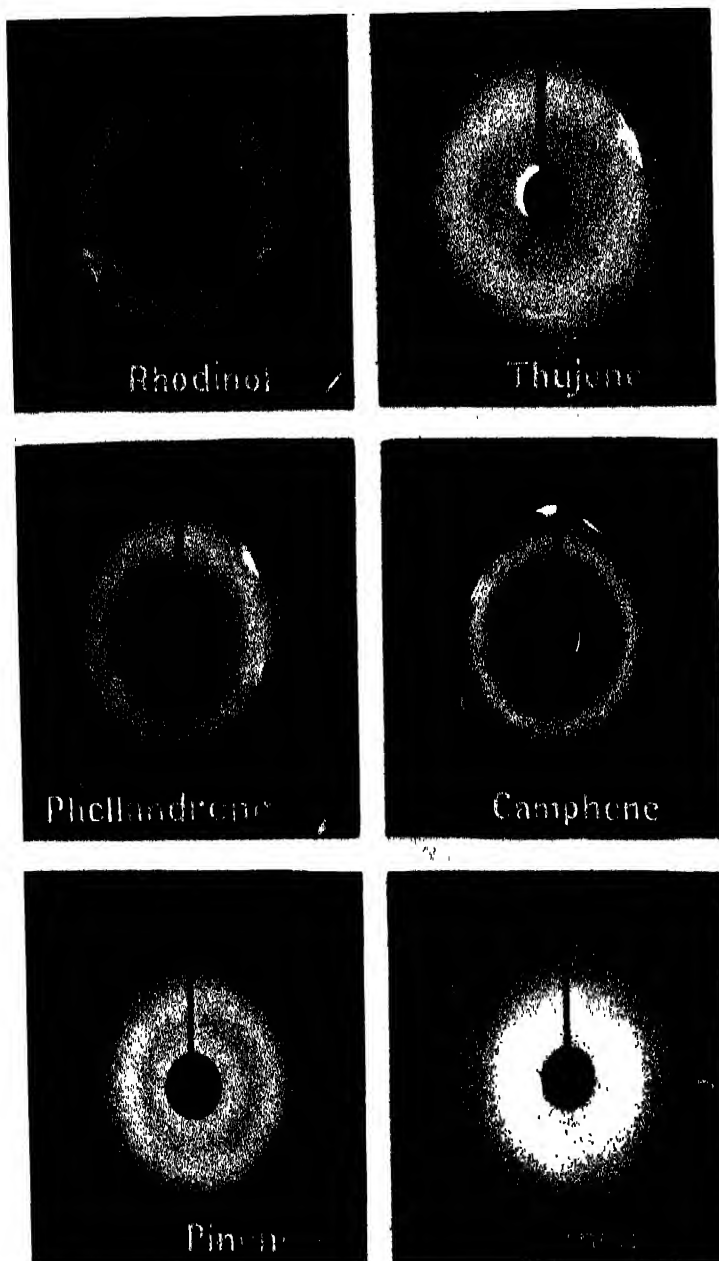
X=Ray Diffraction in Terpenes

Discussion of Derived Results.

1. *Dependence of X-Ray diffraction on the arrangement and structure of molecules.* In order to explain the results, we adopt the fundamental idea of Raman and Ramanathan[1] (*i.e.*, the X-Ray diffraction peaks in liquids occur at wavelengths corresponding to the mean molecular distances between them.

When the molecules are highly asymmetric 2 or 3 haloes may be produced, depending on their relative configurations. These configurations are closely related to the structure of the molecules and consequently the X-Ray patterns too.

The view is also adopted, that depending on the form of the molecule, there are a large number of them arranged in particular configurations.[2]

Thus in a long molecule, the most probable arrangement is on the broadside-on position and the peak of the principal halo corresponds to this intermolecular distance. The lengthwise arrangement in such a molecule has almost no chance and the corresponding peaks are either absent or feeble. When the length of the molecule decreases, the probability of the latter arrangement is enhanced and the inner haloes develop relatively. When the molecule is spherical, all arrangements are equally favoured and a single halo is again produced, the sharpness of the halo depending on temperature and compressibility also. In the case of asymmetric molecules therefore, the relative intensities of the peaks are actually a measure of the relative proportion of molecules arranged in particular configurations at any particular instant. In addition to these molecules, there are also a large number of them arranged at random as shown by the width of the haloes.

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[1] Raman and Ramanathan, Proc. Ind. Assoc. Cult. Sc., 8, 129 (1923).

[2] Sogani and Stewart employ these ideas in slightly different forms to explain the haloes of simple structures studied by them. Morrow introduces the idea of association also.

In the light of these views, diffraction patterns of a few typical cases are discussed and the relation to molecular structure and arrangement is made clear.

As the discussion of 2 typical cases would show the relation between structural symmetry and X-Ray diffraction very clearly, we follow an order slightly different from that in the chart.

Taking first the cases of camphene and pinene (liquids 15 and 16 in the chart) the wide difference between the haloes of these 2 liquids can be understood in view of the structural dissimilarity between them, though they have the same chemical formula $C_{10}H_{16}$. The skeletons of the structures are represented below.

Camphene.
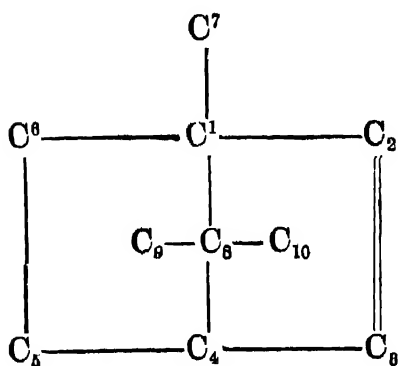
Pinene.
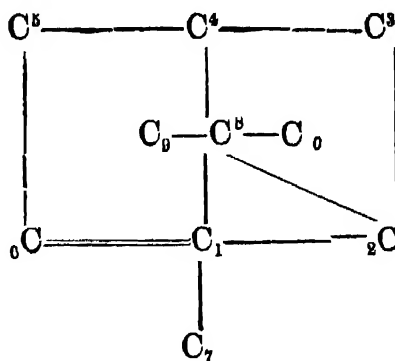
The peculiarly sharp halo for camphene suggests that the molecule is almost symmetrical. Unfortunately we have no data for the compressibility. The 2 distinct edges also indicate, that within certain limits the relative orientation of neighbouring molecules is not definite.

Let us now examine the structure and see if the nature of the halo is consistent with the same. We may roughly

take the carbon atoms in the ring to be almost in a plane and the atoms 10 and 9 at right-angles to the plane of the above ring. Then it is evident that the molecule will have the same diameter and thickness. But the 7th carbon atom will increase the diameter in that direction, if it is in the plane of the ring. On the other hand, the bond between the opposite sides of the ring 1 and 4 will cause a contraction in the same direction. There is also another double bond between 2 and 3. (Regarding the influence of bridging bonds we shall find a similar effect on the structure, in the case of monocyclic compounds also.) Thus the molecule is again nearly symmetrical and this accounts for the nature of the halo.

If we take the 2 margins of the sharp halo as corresponding to the diameter and thickness, $6 \cdot 96 \overset{\circ}{A}$ and $5.19 \overset{\circ}{A}$ respectively, we can compute the density by the formula

$$\rho = \frac{\text{Molecular wt} \times \text{mass of } H \text{ atom}}{\text{diameter}^2 \times \text{thickness}} = 0 \cdot 89$$

in this case. The actual density of d. camphene is $0 \cdot 822$[1]; the density of the d (l) camphene is not known, but the variation between the 2 varieties is generally small and does not interfere with the validity of the general conclusion. The X-Ray patterns of the dextro and laevo compounds, such as pinene and limonene were also found to be identical. This uncertainty therefore does not affect our results.

On referring again to the structure, it will be found that in pinene, it is different from that of camphene. The bridging bond is now between the unsymmetrical carbon atoms 2 and 8 and consequently distorting the ring in a direction different from that of camphene. There is also a double bond between 1 and 6. The 7th carbon atom of the methyl group is now attached in the lower position as represented, but for purposes of our consideration is equivalent to that in

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[1] The densities are taken from the International Critical Tables.

camphene. Thus when compared with camphene the length is greater and the distortion has made the benzene ring highly asymmetrical. In the organisation of the molecules, 2 different arrangements can thus take place. From the relative intensities of the 2 haloes, both arrangements seem to be equally probable. The main ideas and the application of the method can now be extended to the different classes of compounds.

2. *The long chain olefinic terpenes.*—The constant size of the principal halo can be understood if we examine the general structure. The outline of the structure may be represented as

$$C—C—C—C—C—C—OH$$
$$| \qquad \qquad |$$
$$C \qquad \qquad C$$
$$\wedge$$
$$C \quad C$$

This shows that the same kind of molecular arrangement can persist in them along diameter to diameter and consequently they give the same interplanar distance. In linalol (*vide* Chart) the hydroxyl group is changed to the 4th carbon atom and there is a corresponding decrease in the length also of about $1 \cdot 2 \overset{\circ}{A}$. There is no corresponding increase in the diameter (not beyond experimental errors) and this follows as a consequence of the fact that there are already 2 groups normal to the chain as shown in the structure and unless the hydroxyl group has its dimensions larger than those 2 groups, the molecules need not be pushed farther away than their previous positions, due to this structural change. When the hydroxyl groups in geraniol, linalol and rhodinol are changed into the CHO groups in citral and citronellal, the orientative relation in the length to length direction seems to weaken, the inner haloes become faint and there is an increased diffuseness extending up to the principal halo.

If the values a_1 and a_2 be taken to represent the length and diameter, then the density may be computed by the formula

$$\rho = \frac{\text{Molecular weight} \times \text{mass of } H \text{ atom}}{\text{length} \times \text{diameter}^2}$$

For example in geraniol $a_1 = 12 \cdot 6 \overset{\circ}{A}$ and $a_2 = 4 \cdot 22 \overset{\circ}{A}$; the computed density is $0 \cdot 832$ and the actual one is $0 \cdot 881$. From this it appears reasonable to conclude that $12 \cdot 6 \overset{\circ}{A}$ represents the length of the chain approximately. Since the densities of the long chain terpenes vary between $0 \cdot 85$ and $0 \cdot 89$ only, and their molecular wts. are nearly equal, the same kind of agreement may be expected in all of them.

In the case of these long chain compounds, the fact of the decrease in length in linalol also indicates that the OH or CHO groups are in the line of the chain in the other compounds. It is interesting to observe that the faint inner haloes follow the structural changes even more closely than the principal ones.

With a view to obtain information of the increase in diameter in these long chain terpenes due to the attachment of the side groups normal to the chain, N. hexane C—C—C—C—C—C was investigated. The diameter obtained was $4 \cdot 54 \overset{\circ}{A}$, whereas the average value for the terpenes is $4 \cdot 93 \overset{\circ}{A}$. This increase of $0 \cdot 4 \overset{\circ}{A}$ is the aggregate effect of the unsaturated isopropyl and the methyl group over a normal hydrocarbon chain. It is interesting to compare this result with that of Stewart[1] for isomers of normal heptane and alcohols. In the latter case he finds that a methyl group normal to the chain contributes $0 \cdot 6 \overset{\circ}{A}$ to the diameter and in the former $1 \cdot 04 \overset{\circ}{A}$. This value $1 \cdot 04 \overset{\circ}{A}$ is also not constant as observed by him.

[1] Stewart, Phys. Rev. 32, 158 (1928).

camphene. Thus when compared with camphene the length is greater and the distortion has made the benzene ring highly asymmetrical. In the organisation of the molecules, 2 different arrangements can thus take place. From the relative intensities of the 2 haloes, both arrangements seem to be equally probable. The main ideas and the application of the method can now be extended to the different classes of compounds.

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For example in geraniol $a_1 = 12\cdot6\overset{\circ}{A}$ and $a_2 = 4\cdot22\overset{\circ}{A}$; the computed density is 0·832 and the actual one is 0·881. From this it appears reasonable to conclude that $12\cdot6\overset{\circ}{A}$ represents the length of the chain approximately. Since the densities of the long chain terpenes vary between 0·85 and 0·89 only, and their molecular wts. are nearly equal, the same kind of agreement may be expected in all of them.

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[1] Stewart, Phys. Rev. 32, 153 (1928).

3. *Terpineol.*—The peculiar interest of the haloes of this liquid lies in its chemical relation to pinene on the one hand, and geraniol on the other. It can be obtained by dehydration of pinene and by the action of acetic acid on geraniol.

It will be seen from the table and the structures given below, that though there is a ring formation
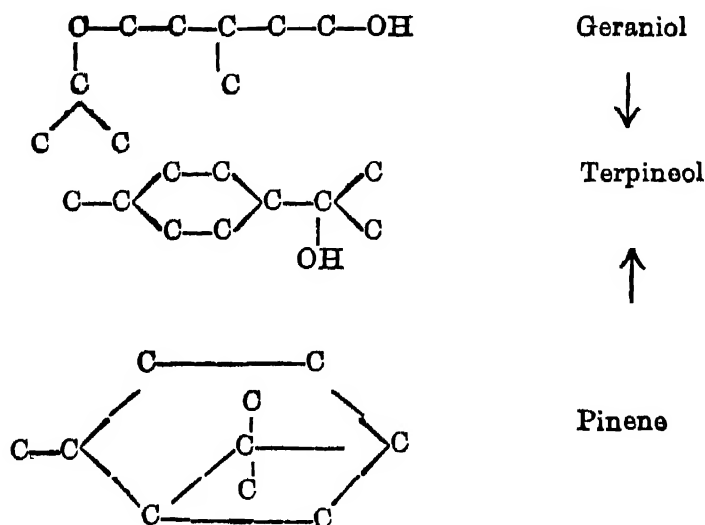
from geraniol to terpineol the increase in diameter is only 0.16Å. This is not difficult to understand, for the geraniol chain has 2 groups normal to it, contributing to the diameter, but during the ring formation, they have now moved to the opposite corners increasing as though the length of terpineol. Thus for purposes of X-Ray diffraction, we may consider terpineol as almost equivalent to a long molecule. It is evident from the structural representation that the OH group cannot contribute to the length. The actual length as given by the present data is 10.9Å. If the OH group also had contributed to the length, then the total length would be $(10.9+1.2)\text{Å}$. (The latter value for OH is the one obtained from the case of linalol.) This would make terpineol nearly as long as geraniol, whose length is 12.8Å.

We thus see that the decrease in length due to the ring formation is nearly compensated by the opposite positions of the groups. This consideration will be of use to us in the case of ring compounds discussed later.

The length of terpineol being smaller than that of geraniol, there is an increased probability of the length to length arrangement, and this is seen in the enhanced intensity of the inner halo relative to that of geraniol.

Taking the values $10 \cdot 9 \overset{\circ}{A}$ and $5 \cdot 08 \overset{\circ}{A}$ to represent the length and breadth of terpineol, if we compute the density by the usual formula $\rho = \frac{\text{Molecular wt.} \times \text{mass of H atom}}{\text{length} \times \text{diameter}^2}$ it comes out as $0 \cdot 921$. The average density of the dl, $d(l)$ and β terpeneol is $0 \cdot 890$. The ordinary variety that is obtained is a mixture and this was investigated in the present case. In pinene, the benzene ring has undergone considerable changes due to the bridging bond and the position of the various groups inside. The diameter has increased by $1 \overset{\circ}{A}$ relative to terpineol. The length is now smaller than the latter liquid by $0 \cdot 8 \overset{\circ}{A}$, but it will be observed that the C_3H_7 group contributing to the length of terpineol is absent in pinene, being situated within the ring. When this is taken into account, it would appear that the ring is highly distorted along the lengthwise direction also, as indicated before.

Corresponding to the diminution in length relative to terpineol, the lengthwise organisation of the molecules in pinene has become more probable and this is found in the larger intensity of the inner halo compared with that of terpineol.

The gradual diminution in length and the correspondingly enhanced intensity of the inner haloes of these 3 allied liquids, makes it reasonable to attribute them to the same causes as the outer ones.

4. *Cyclic terpenes with a CO group in the ring* : Menthone, carvone and thujone.—For purposes of X-Ray
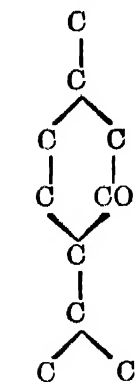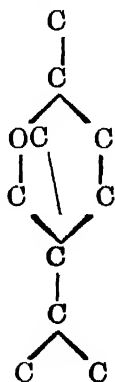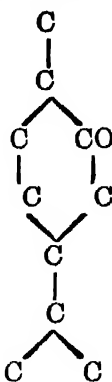
Menthone   Thujone   Carvone

diffraction we may consider these compounds as benzene with groups as indicated. When the groups are in the paraposition, just as in the case of terpineol, previously considered, this is again almost equivalent to a long chain compound. The molecules will mostly be arranged on the broadside-on position and there will be a single halo corresponding to this distance. But when a group is substituted in the ortho- or meta-position, then it does not correspond to a long chain molecule, for the ring is elongated unsymmetrically and a thickness and a diameter to diameter arrangement become possible in the organisation of the groups. Two haloes are thus produced. The observations of Krishnamurti[1] on disubstituted benzene derivatives may be recalled in this connection. In the case of menthone, the presence of the oxygen atom in the meta-position (corresponding to the CH_3 group) may be considered equivalent to a small group. The asymmetry is of course small, for the oxygen atom has only 8 electrons. There is a faint halo at smaller angles indicating that there are a small number of molecules arranged diameter to diameter, this being a mean value approximately in the plane of the ring. In the case of

[1] Krishnamurti, Ind. Jour. Phys. 2, 355 (1928).

carvone, the faint halo is however not seen, but the primary halo is very diffuse, and the same considerations as those of long chain terpenes apply here.

Thujone stands separately in giving a sharp halo relative to the other two. It will be found from the structural representation, that there is a bond between the carbon atoms in the unsymmetrical corners. Such bonds do not exist in benzene derivatives. From the considerations of pinene and camphene, it was evident that such bonds had a distorting influence on the structure. This exceptional behaviour of thujone relative to the two allied compounds lends support to that view. The bridging bond in thujone seems to compensate partially for the asymmetries produced by the groups and the halo approaches closer to that of compounds possessing structural symmetry.

Chemically these compounds are not benzene derivatives, and small structural changes of the ring of the compound itself must be considered for a strict comparison.

5. *Cyclic terpenes* $C_{10}H_{16}$ (1) Terpinene, (2) Dextro limonene, (3) $d(l)$ Limonene, (4) Dextro a Phellandrene, (5) Sylvestrene, (6) Camphene, (7) Dextro-pinene and (8) Laevo pinene.—The last 3 liquids have been considered previously. Of the first five liquids, only sylvestrene has the group in the meta-position and consequently it has a faint halo at smaller angles. The reason for this will be obvious, because the ring is unsymmetrically elongated and in the organisation of the groups, 2 arrangements have become probable. The other 4 monocyclic terpenes have the same structure

Sylvestrene
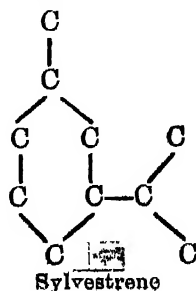
with the groups in the para-position and are thus comparable to long chain hydrocarbons. They have therefore generally one halo. The orientative relation however seems to be better as shown by the decrease in the diffuseness of the haloes, when compared with long chain terpenes.

6. *Sesquiterpenes* $C_{15}H_{24}$: Cadinene, inene, caryophyllene and cedrene.—From the foregoing considerations, it is not difficult to find an explanation for the 3 haloes of these liquids. Unfortunately the exact structure of the compounds is not known. But most of them are known to possess a naphthalene ring with side groups. One of them, namely inene, was very recently isolated by Prof. P. C. Mitter of the University College of Science. The structures are somewhat as represented below.
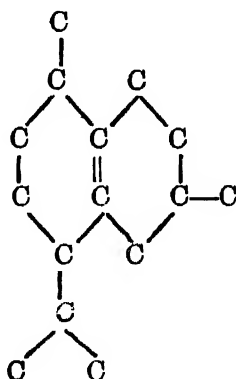
For purposes of X-Ray diffraction, the left-hand side, may be compared to a para-substituted benzene derivative or corresponding to a long chain compound. As will be seen from the structure, there is a large asymmetry due to the right-hand side ring with another side group in the corner of the latter and two haloes may be expected. But if any of the groups change to the meta- or ortho-position, two haloes may be attributed to this configuration alone as in benzene derivatives. The third spacing which is the outermost halo, and corresponding to the thickness of the molecule, is not

likely to be influenced by these changes of positions of the groups. This is shown in the diffuse haloes between 15° and 25° remaining practically constant in all of them. If the molecule were perfectly flat and possessed a definite arrangement from thickness to thickness, we would expect a distinct maximum instead of the diffuse halo as obtained here. This halo indicates that the orientative influence is not definite, but allows of a wide margin, shown by the limits of the haloes. From the chemical standpoint, these liquids are not exactly naphthalene derivatives and the analogy cannot be pushed too far, without taking into account other structural changes in the naphthalene ring itself. It is however interesting in this connection to compare the diffuse haloes of these liquids, with that of liquid naphthalene between 18·1° and 26·9° shown in the chart given by Herzog and Jancke.[1]

In conclusion, I have great pleasure in acknowledging my heart-left thanks to Prof. C. V. Raman, F.R.S., for the kind suggestions and directions during the course of the investigations. My thanks are also due to Prof. P. C. Mitter, for his kindness in placing at my disposal pure samples of these liquids and advice on chemical aspects.

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210, BOWBAZAR STREET, CALCUTTA.

Herzog and Jancke, Zeit. fur, Phys. 45, 194 (1927).

Influence of Temperature on the X-Ray Liquid Haloes

By

V. I. VAIDYANATHAN, M.A.

Re search Scholar in the Indian Association for the Cultivation of Science.

Plate XXI.

ABSTRACT.

X-ray diffraction haloes of five liquids, camphene, mesitylene, acetic acid, butyric acid and ethyl alcohol have been studied at two different temperatures. Camphene has only a single halo, whereas the others have two. The following effects, namely; an increase in the scattering at small angles, a contraction of the haloes and an increase in their diffuseness have been observed in all cases. In addition to these effects, in the case of liquids with two haloes, it is noticed that with rise of temperature, the separation between the inner and the outer halo tends to be effaced and that the inner haloes become diffuse more quickly than the outer ones. In the case of acetic acid, butyric acid and ethyl alcohol, which are known to be associated at ordinary temperatures and also dissociated at higher temperatures, these effects are specially striking.

The various phenomena are interpreted on the basis of the theory of Raman and Ramanathan.

Introduction.

Though the X-ray diffraction patterns of many liquids have been examined at ordinary temperatures, very little

work has been done on the changes produced in them by high temperatures. Ramasubramaniam [1] made some preliminary studies at Calcutta on the subject. A more detailed examination of the phenomena appeared desirable, specially of those cases in which more than one halo appears in the diffraction pattern of the liquid.

Such double haloes have been observed in many liquids of the aromatic series. Krishnamurti [2] has observed them in all ortho and meta-substituted benzene derivatives, the intensities and sizes of the inner haloes varying considerably. Thus in o-cresol and guiacol, the inner haloes are more intense than the outer, whereas in ortho-nitrobenzaldehyde, the two haloes are of nearly the same intensity, and in methyl anthranilate the outer halo has increased in brightness relative to the inner.

Liquids with two haloes where the inner ones are as intense as the outer have also been obtained by Sogani [3] in many liquids as o-nitrotoluene, m-nitrotoluene, and mesitylene.

Katz [4] finds similar intense inner haloes in 1.3.5 trimethyl benzene (mesitylene) 1.3.4 trimethyl benzene, 1.2.3 trimethyl benzene, triethyl benzene, trimethyl pyridine and many other liquids.

On the other hand, the inner haloes in normal primary alcohols, fatty acids, etc., are much fainter than those of the previous class. These have been systematically investigated by Stewart and others.[5]

In the former class of compounds, it has been suggested that the haloes correspond to the dimensions of the molecule, whereas in the latter it has been supposed that the inner haloes are due to association.

[1] Ramasubramaniam, Ind. Jour. Phys. 3, 137 (1928).

[2] Krishnamurti, Ind. Jour. Phys. 2, 355 (1928).

[3] Sogani, Ind. Jour. Phys. 1, 357, 1927 and 2, 97 (1927).

[4] Katz, Zeit. fur. Phys. 46, 392, (1928).

[5] Stewart and Morrow, Phys. Rev. 30, 232 (1927) (See also Morrow, 31, 10, 1928).

The influence of temperature on the X-ray haloes may also help us to understand these phenomena more clearly. As typical of the different classes of liquids; ethyl alcohol, acetic acid, butyric acid, mesitylene and camphene are studied at two different temperatures.

Experimental.

The diffracting wave-length was CuK_a. The liquids were sealed in glass tubes having the minimum thickness of the walls, necessary to withstand the vapour pressure generated by heating the liquids. The diffraction effect of the glass walls of the containing tubes was tested by giving blank exposures, without the liquid. In the negatives obtained for camphene, which is known (in mica containers) to give a very clear space inside the primary halo, there was a faint halation round the central disc and extending a little beyond, produced by the glass walls of the tube. This effect was however not so intense as to confuse the diffraction pattern of the liquids in most cases, to any appreciable extent. The same glass tube was employed for the pictures of the hot and cold liquids and it was not disturbed in any way during the experiments. When the patterns for the heated liquids were taken, it was found necessary to keep the photographic plate cool, by blowing cold air into the camera and circulating ice-cooled water behind the slides.

Results.

In calculating the results, the well-known Bragg formula is applied. In the table given below, a_1 corresponds to the principal halo and is the diameter of the molecule, a_2 is the corresponding length calculated from the peak of the inner halo. The higher temperatures are accurate to within five degrees and the lower two degrees.

Liquid.	Temperature.	a_1 $\overset{\circ}{A}$	a_2 $\overset{\circ}{A}$
Camphene	30	5·76	
	185	6·05	
Mesitylene	80	3·68	7·4
	150	3·84	
Acetic acid	28	4·22	7·2
	130	4·48	
Butyric acid	80	4·63	9·7
	120	4·80	10·2
Ethyl alcohol	30	4·16	7·8
	145	4·37	

As will be seen from the results, the haloes contract on heating the liquids, the inner as well as the outer. This behaviour is found to be similar in mesitylene, ethyl alcohol, and the two acids. Camphene has only a single sharp halo, which also contracts similarly as the outer haloes of other liquids. The haloes appear more diffuse in the hot than in the cold. This effect seems to be even more prominent in the inner haloes than the outer. Because of this effect, the location of the peak of the inner maxima in the hot patterns of the liquids was not possible and the corresponding measurements are not therefore given except for butyric acid, where the position could be located more or less reliably. The space separating the central disc from the inner haloes in the cold picture has filled up in the hot pattern. This effect is strikingly noticed in ethyl alcohol and acetic acid, whereas in butyric acid, the separation of the central spot from the

Cold   Hot

Ethyl   Alcohol

Acetic   Acid
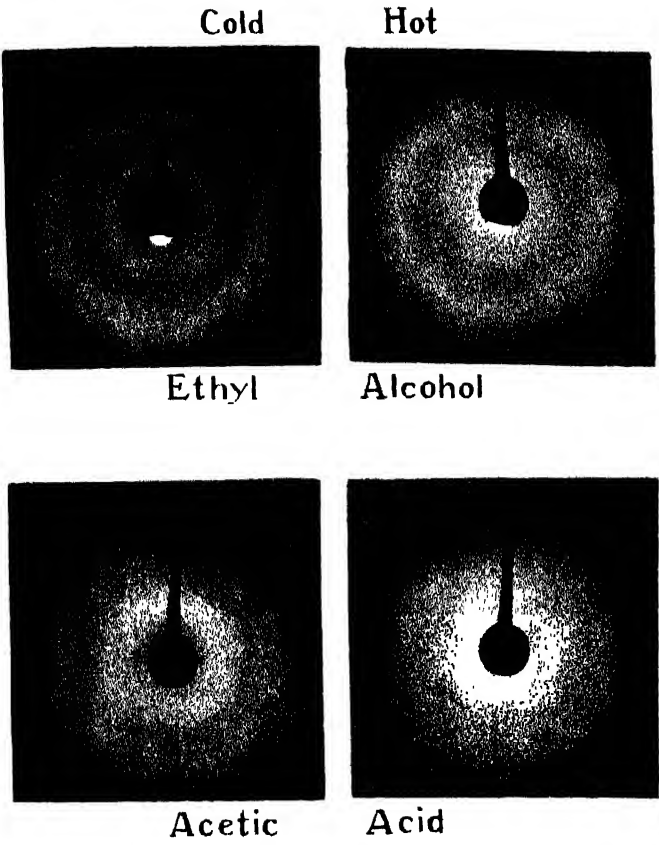
Thermal Effect on the X=Ray Haloes

inner halo continues to be still visible in the negatives, though not very clearly. In mesitylene, this separation is not distinct even in the cold picture and hence this effect could not be clearly seen. Another interesting observation that arises where we have the two haloes is that, the separation between the inner halo and the outer tends to be effaced in the hot patterns. This is again very clear in ethyl alcohol and acetic acid and to a lesser degree in mesitylene and butyric acid. The haloes for mesitylene are diffuse even at ordinary temperatures, and so it is difficult to observe this phenomena. But on a close examination of the negatives, these effects are seen to be present. An important feature is the increase in the general scattering throughout and within the halo, on rise of temperature. In camphene which has only a single halo, this effect is very clearly seen. In other liquids, this effect is superimposed on the inner haloes and manifests itself as an increase in the intensity of the latter, in spite of their becoming more diffuse at higher temperatures.

Discussion of Derived Results.

These phenomena may be understood in the light of the theory of Raman and Ramanathan.[1] Three effects have been predicted by the theory, as a consequence of the rise of temperature. (1) An increase in scattering at small angles with the primary beam, (2) an increase in the diffuseness of the halo, and (3) a contraction of the radius of the halo.

The first effect is a consequence of the fact that at very small angles, the considerations of optical scattering may be applied to the case of X-ray. Though when the angle of scattering θ has any moderate value and the diffracting wave-

[1] Raman and Ramanathan, Proc. Ind. Assoc. Cult. Sc., 8, 129 (1928).

length is of molecular dimensions, the considerations of optical scattering are not applicable, it is shown that in the former case, when θ is very small, the Einstein-Smoluchowski theory holds in the X-ray scattering. It is well-known that optical scattering increases with increase of temperature.

The second effect may best be understood from the expression that has been derived by these authors, for the intensity of scattered radiation in any direction θ which is as follows:

$$I = C_1 \cdot \text{Exp.} \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0^3 \left(1 - \frac{\lambda_1^2}{\lambda_0^2} \right)^2 \right\}$$

where R and N are the gas and Avogadro constants, T the absolute temperature, β the isothermal compressibility and λ_1 is given by the usual expression $\lambda = 2\lambda_1 \sin \frac{\theta}{2}$, λ_0 is the mean molecular distance and C_1 a constant. It would be seen from the expression that since both T and β are involved in the exponential, the intensity curve would be flatter when graphed at the higher temperature than at the lower. When T increases both T and β increase.

The contraction of the radius of the halo is easy to understand. For when the medium is heated, the liquid expands and consequently the inter-molecular distance increases.

Since the theory has been derived for the case of a simple molecule giving rise to a single halo, these general expectations may be verified in camphene. The diffuseness of the halo increases, but it is not so striking as the other effects. This depends also on the compressibility of the medium and since we have no data, it is not possible at present to make a quantitative verification of the expression.

It is not surprising however, that these general effects are found to hold in the case of liquids with two haloes also, though the theory is not strictly applicable in this case.

If we now suppose that the two haloes arise because the local distribution of molecules around any molecule is not symmetric and depends on the form and symmetry of the molecule,[1] the other phenomena regarding the inner haloes may also be understood. Thus if we take a long molecule like hexane, a larger number of molecules may be assumed to lie on the broadside-on position than on the end-on position. The latter arrangement has almost no chance, the corresponding inner halo being feebler or absent. There is also another factor to be taken into account in the present case, *i.e.*, the question of polarity of molecules. If we compare two liquids like hexane and primary n. hexyl alcohol, the lengths of the molecules are nearly the same, but in the former case, there is only a single diffuse halo, whereas in the latter, there is found to be an inner halo also.[2] It will be observed that primary n. hexyl alcohol has a polar group. Thus the polarity also seems to have an influence on the local distribution of molecules. If the medium is now heated, the molecules attain a larger degree of freedom of motion and the distribution tends to become more and more symmetric. The two haloes consequently tend to unite. The lengthwise arrangement in a long molecule being obviously less stable, this tends to get disturbed sooner and the inner haloes consequently become more diffuse relative to the outer.

In connection with the behaviour of the inner haloes, it is also interesting to draw attention to the recent work of Ramachandra Rao [3] on light-scattering in liquids at different temperatures. He finds that the value of the optical anisotropy calculated from the depolarisation factor, generally increases in normal liquids. This increase was found to be quite uniform

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[1] On the assumption that the distribution of molecules around any molecule depends on its form and symmetry, a theory of light-scattering in liquids has been discussed in a recent paper by Raman and Krishnan, Phil. Mag. 5, 498 (1928).

[2] Stewart and Skinner, Phys. Rev. 31, 1 (1928).

[3] Ramachandra Rao, Ind. Jour. Phys. 2, 179, 1928 ; 3, 1 (1928).

in carbon tetrachloride, hexane, etc., whereas in methyl acetate, ethyl formate, chorobenzene and other liquids, there was an increase though not so uniform. On the other hand, in butyric acid, acetic acid and propionic acid, this factor showed a rapid fall up to about 70°, 120° and 100° C respectively, after which they also behaved as normal liquids. In ethyl alcohol there was a fall at about 140°C, though not so strikingly as in the acids. He suggests that this extraordinary behaviour may be due to molecular association in these liquids.

In the present investigation also we are concerned with a similar phenomenon. If the inner haloes are due to associated molecules at ordinary temperatures, we may naturally expect them to be absent in the hot patterns. In view of the foregoing facts and considerations, it may be suggested that the polarity affects the distribution of molecules and consequently we have two haloes depending on the same. The inner haloes may not be the direct consequence of association of molecules.

In conclusion, I have much pleasure in acknowledging my heart-felt thanks to Prof. C. V. Raman, F.R.S., for his kind suggestions and directions during the course of the investigation.

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X-Ray Diffraction in Liquid Alloys of Sodium and Potassium.

BY

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ABSTRACT.

The theory of Raman and Ramanathan for X-ray diffraction in liquids is found to explain the nature of the haloes for liquids with symmetrical molecules nicely and hence is applied for the interpretation of the experimental results. A series of X-ray diffraction haloes produced by liquid alloys of sodium and potassium having different proportions have been studied. The alloy is regarded as a solution of the excess of either of the metals dissolved in the liquid compound Na_2K, and the results are discussed in accordance with the results of Krishnamurti for X-ray diffraction in aqueous solutions. When the amount of the dissolved metal is small compared to the amount of the solute Na_2K, the halo is nearly the same as that given by Na_2K and when either of the metals proponderates to a large extent the halo is practically the same as that given by the metal. In the intermediate stages the effect may be regarded as a superposition of the effects due to Na_2K and the metal in excess. From the size of the halo for Na_2K obtained graphically it appears that the three atoms of this compound are placed at the corners of a triangle. A faint inner ring is observed in cases where the excess of either of the metals in Na_2K is small.

1. *Introduction.*

Sodium and potassium form a series of alloys which are liquid at ordinary temperatures. From his observations on the heats of formation of these alloys, A. Joannis[1] concluded

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[1] A. Joannis, Ann. Chim. Phys. (6), **12**, p. 358, 1887.

that a compound represented by the formula Na_2K is formed. On the contrary, N. S. Kurnakoff and N. A. Puschin[2] found from the variation of the fusion points of these alloys that the compound that is formed by the combination of Na and K has the composition represented by the formula Na_nK, where n has a value greater than 1.45. He also found that the composition corresponding to the formula NaK represented an eutectic point. G. van Bleiswyk[3] found that the value of n is 2 and the compound represented by this formula is the only compound that is formed. It may thus be considered that when an alloy of sodium and potassium contains an excess of either of the metals over that required by the formula Na_2K, the excess remains dissolved in this compound. In view of the recent investigations regarding the relation between X-ray diffraction halo due to a liquid and its molecular structure, these liquid alloys may very profitably be investigated by examining the X-ray diffraction haloes formed by them.

Extensive studies on the subject of X-ray diffraction in solutions and mixtures have been made in Calcutta by Mr. P. Krishnamurti and are described in a series of papers contributed to the Indian Journal of Physics. In his first communication[4] Krishnamurti investigated the case of concentrated solutions of ammonium nitrate and acetamide in water. In his second paper[5] he has investigated the diffraction haloes by different kinds of sugar solutions. The general results indicated by this and other later investigations of his appearing in the current issue of this Journal is that the pattern due to very dilute solutions is that of the solvent upon which appears superposed a corona or gaseous scattering due to the molecules of the dissolved substance. In more con-

* K. S. Kurnakoff and N. A. Puschin, Zeits. Anorg. Chem., 30, p. 109, 1902.
* G. van Bleiswyk, Zeits. Anorg. Chem., 74, p. 152, 1912.
* P. Krishnamurti, Ind. Journ. Phys., Vol II, pt. IV, p. 501, 1928.
* *Ibid*, Vol. III, pt. II, p. 209, 1928.

centrated solutions the corona due to the dissolved molecules gives place to a diffraction ring which in some cases appears in the pattern more or less independently of that of the solvent, and in others join up with it and modifies its position. We may if we so choose, consider the alloy of sodium and potassium as a solution of the excess of either metal in the compound Na_2K and apply the results of Krishnamurti in order to interpret our observed phenomena.

Before we proceed further, however, we must first decide upon the correct point of view regarding the origin of X-ray diffraction in liquids. Stewart[6] has recently discussed the theories of X-ray diffraction in liquids and has pointed out that the thermodynamic theory of Raman and Ramanathan[7] put forward in 1923, offers a satisfactory explanation of at least some of the outstanding facts of observation. It is based on the Principle of Boltzmann which was applied by Smoluchowski and Einstein to explain the phenomenon of the critical opalescence in liquids. At ordinary temperatures, the compressibility of liquids is small and hence the fluctuations of density are small. From this it readily follows that at small angles of scattering, the medium may be considered as a uniform continuum which gives rise to no scattering, except to the limited extent due to the thermal fluctuations of density. This is in agreement with observations. At larger angles of scattering the discrete structure of the medium begins to play an important part. The smaller the fluctuations the more uniformly spaced are the molecules, and hence at a suitable angle of diffraction, give rise to a halo which is the more sharply defined when the deviations from uniformity of the molecular spacing are smallest, *i.e.*, when the compressibility is least. The extension of the thermodynamical considerations which determine the fluctuations of density to

Stewart, Phys. Rev., Vol. 32, p. 588, 1928.
Raman and Ramanathan, Proc. Ind. Ass. Cult. Sci., Vol. VIII, p. 127, 1923.

find the variations in the spacing of the molecules appears legitimate in view of the general validity of the Boltzmann Principle. The success of the Raman-Ramanathan theory is very strikingly shown in the case of liquids with simple monatomic molecules as for example liquid mercury, which gives a diffraction halo in which the scattering at small angles is extremely small, and the halo is very well-defined, as might be expected from small compressibility of mercury. The distribution of intensity calculated according to Raman-Ramanathan equation

$$I_{\lambda_1} = C_1 \exp. \left\{ -\frac{1}{16} \frac{N}{RT\beta} \lambda_0{}^3 \left(1 - \frac{\lambda_1{}^3}{\lambda_0{}^3} \right)^2 \right\} \qquad \dots (1)$$

λ_1 for different angles being obtained from the relation

$$\lambda_1 = \frac{\lambda}{2 \sin \frac{\theta}{2}} \qquad \dots (2)$$

The second and third diffraction bands obtained by Prins[6] may be regarded as the second and the third order diffraction effects and for finding the intensity distribution we write instead of C_1, C_1' and C_1'', respectively as the constants for the second and third order effects corresponding to C_1 in equation. (1). The diffraction haloes of the higher orders are also given by equation (1), by taking instead of λ_1 as given by equation (2), λ_1' and λ_2' respectively as given by

$$\lambda_1' = \frac{2\lambda}{2 \sin \frac{\theta'}{2}} \qquad \dots (3)$$

$$\lambda_1'' = \frac{3\lambda}{2 \sin \frac{\theta''}{2}} \qquad \dots (4)$$

Prins, Physika, 6,351 (1926).

The agreement of the theoretical distribution of intensity with the photographs of Prins for diffraction of X-rays by mercury is remarkable. The experimental results, namely, the sharpness of the first band, the greater width of the second band, the diffuseness of the third band, and also the rapid rise of intensity to the maximum values at smaller angle side, specially in the case of the first maximum, appear very nicely in the theoretical curve (Fig. I).

ANGLE OF DIFFRACTION
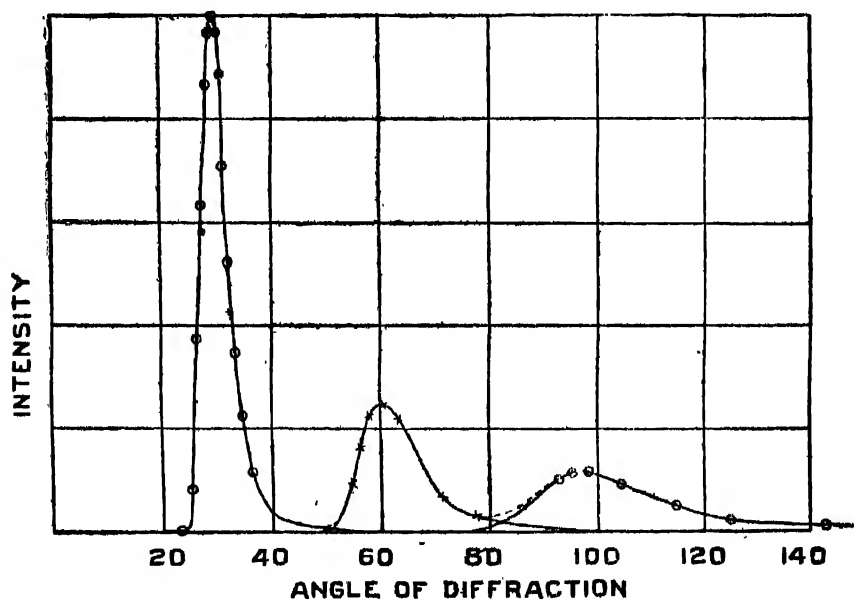
FIG. I

2. *Experimental Arrangements.*

The X-ray tube used for the experiment was one of the Shearer type run by an induction coil. The current through the tube was about 5ma. The antikathode was made of molybdenum and a thin sheet of aluminium was used for the window. The rays were allowed to pass through a zirconium oxide screen which cuts off the K-radiation by 60 per cent. so that the beam was sufficiently monochromatic. The camera was similar to that used by C. M. Sogani.[9] The nature and

⁹ C. M. Sogani, Ind. Journ. Phys., Vol. I, pt. IV, pp. 357-92, 1927.

dimensions of the hole through which the beam was allowed to pass were the same, but the size of the camera was bigger. The distance of the photographic plate from the material irradiated being 7·35 cm. The alloy was placed in narrow flattened glass tubes of thicknesses varying from half a millimetre to one, and the width lying between 2 to 3 mms. The walls of the glass tubes were so thin that no diffraction pattern due to glass was formed on the photographic plate for a longer exposure in a test experiment.

The alloys were prepared by heating the mixture of the two metals in transformer oil. The substance was introduced into the glass tubes by suction by means of a rubber bulb attached to an end of the glass tube and both ends were sealed off before putting it into the camera. The alloy was analysed gravimetrically by converting it into the chlorides and then into the perchlorates. The composition was estimated by treating the mixture with absolute alcohol which dissolves the $NaClO_4$ leaving the potassium salt. The result was checked by a volumetric analysis depending on the estimation of chlorine in the chlorides of the two metals by silver nitrate solution of known strength.

3. *Discussion of the Results.*

The results that were obtained for alloys of different proportions of the metals are shown in the following table :—

Percentage of Sodium.	Atomic Percentage of Sodium.	Diffracting Angle.	Spacing in A.U.
67·1	78·0	12°24′	3·29
62·2	74·1	12°1′	3·39
55·6	68·6	11°45′	3·47
49·4	63·0	11°37′	3·51
34·6	47·9	11°28′	3·55
24·2	39·2	11°7′	3·66

The figures in the last column of the table represent the spacing of the diffracting centres according to Raman-Ramanathan theory by the Bragg formula

$$a = \frac{\lambda}{2 \sin \dfrac{\theta}{2}}$$

where λ is the wave-length of the X-ray and θ is the angle of diffraction.

The results are represented graphically by drawing a curve between the percentage of sodium and the diffracting angle. The values of the angles of diffraction by pure sodium and potassium are obtained from the results of Keesom [10] after modifying for the change of density at the temperature of the experiment, and are taken to be 12°36′ and 10°22′ respectively. These are the points A and B in the graph.

On examining the graph it is observed that there is a point of inflection at the point C roughly corresponding to

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[10] Keesom, Proc., Roy. Acad., Amsterdam, Vol. 30, p. 341, 1927.

the composition represented by Na_2K. The spacing of the
diffracting centres corresponding to this position is 3·48 Å
which is intermediate between those for pure sodium and
potassium in the liquid state. Thus the corresponding angle
11°40′ is the angle of diffraction for molybdenum K_α rays by
the liquid compound Na_2K. As the amount of sodium is
increased, the angle of diffraction increases till the value 12°36′
for pure sodium in the liquid state reached. Similarly, the
angle decreases with the increase of potassium till the value
10°22′ for pure potassium is reached.
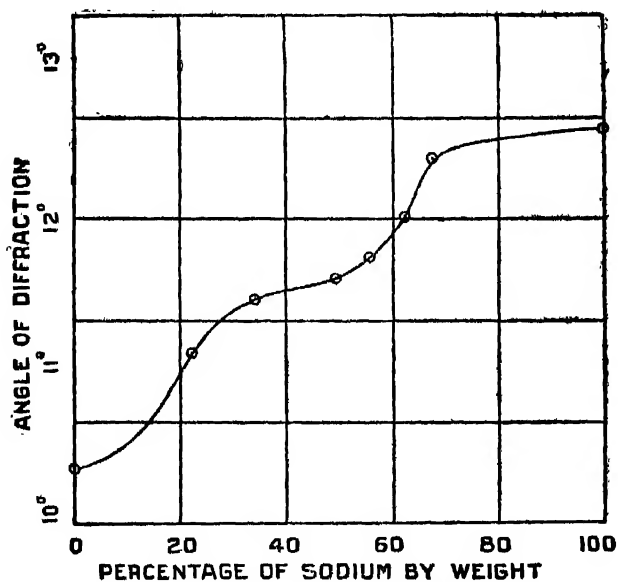
FIG. II

The nature of the variations of the angle of diffraction
will be clear when we remember the results of Krishnamurti.[11]
The point of inflection on the curve for the composition given
by Na_2K shows definitely that a compound of that composition
is formed and the diffraction ring changes slowly in diameter
with additions of either of the metals in it near about this
composition. But as the amount of sodium is still increased

[11] Krishnamurti, loc. cit.

the angle increases and the effect may be regarded as a super-position of the diffraction patterns due to Na and Na_2K. This agrees with the results of Krishnamurti who finds that for extremely concentrated solutions the diffraction patterns given by a substance in solution is similar to those given by the dissolved substance itself. The nature of decrease of the angle of diffraction for increase of potassium is also similar. Since no point of inflection is present on the curve at points corresponding to compositions represented by NaK or NaK_2 these two compounds are not probably formed. The observations are not, however, sufficiently numerous to make this assertion with definiteness.

In the compound Na_2K two sodium atoms are attached to a potassium atom in a molecule. The obvious way in which this can happen are either, that the atoms of sodium are placed at the two sides of the potassium atom diametrically opposite to one another, or that the three atoms may form a triangle with one atom at each corner. If the latter view be taken we have the case of a flat molecule of Sogani[12] and the spacing should be determined by its so-called thickness, i.e., by the distance between the centres of scattering of the molecules when they are placed side by side. The spacing of this compound should thus be intermediate between those for sodium and potassium, which has been found to be the case actually. On the other hand, if the other view be taken the molecule becomes an elongated molecule of Sogani.[13] The spacing of diffracting centres should in that case be determined by the diameter of cross-section and since the diameter of the potassium atom is larger than that of either of the sodium atoms, the spacing should be determined by the diameter of the potassium atom. Hence, in this case, in order to reconcile with the experimental fact that the spacing is closer for Na_2K than for potassium, we are forced to make

[12] C. M. Sogani, Ind. Journ. Phys., Vol. II, pt. I, p. 117, 1927.

[13] Ibid, p. 112.

the assumption that the potassium atom is elongated to a very considerable extent and thereby reduced in cross-section by the attraction of the sodium atoms, which is *prima facie* a forced assumption and hence does not in all probability represent facts.

In the photographs of the three cases in which the amounts of sodium are 55·6, 49·4 and 34·6 per cent. an inner ring in each case was visible but it was extremely faint and diffuse. The diameter could be measured only in one case in which the amount of sodium was 49·4 per cent. and the corresponding angle of diffraction was 6°31'. The ring is thus only visible when the alloy does not contain a large amount of excess of sodium or potassium over that required by the formula Na_2K and it becomes more and more diffuse and indistinct due to admixture of the free metals.

It is interesting that in all the plates the rings are very sharp with very little scattering inside for the cases where there were no inner rings. This is what is to be expected when the amounts sodium or potassium is predominantly large in view of the monatomic nature of the molecules. In the cases where the amount of Na_2K was considerable, due to the presence of the inner ring, it was not possible to see whether there was any internal scattering or not. The outer rings were, however, very sharp.

The Kerr effect in viscous liquids due to radio frequency oscillating field.

By

S. C. SIRKAR, M.Sc.

ABSTRACT.

The Kerr effect in viscous higher alcohols has been studied for radio frequency oscillating field.

A peculiar kind of restoration of light between crossed nicols is observed which is a phenomenon entirely different from the Kerr effect and is most conspicuous in the region of frequencies in which there is strong electric absorption.

The liquid becomes translucent in the electric field at such frequencies.

The Kerr effect in undecyl alcohol is observed to become too small to be observed for an oscillating field of wave length 114 cm. showing the existence of a time of relaxation in the Kerr effect which lies between 10^{-8} to 10^{-9} sec. for this alcohol.

Introduction.

It is a well-known fact that a liquid becomes doubly refracting under the action of a strong electric field. This phenomenon was discovered by Kerr[1] in 1875 and is called the Kerr effect. If the field acts at right angles to a parallel beam of light passing through the fluid and if the light be polarised at 45° with the field, its two components parallel and perpendicular to the field travel with different velocities so that on emergence they combine to form an elliptically polarised beam. The analysing nicol placed so as to quench the beam, can no longer quench the elliptically polarised beam

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[1] J. Kerr, Phil. Mag. (4) 337, 446, 1875.

and the field of view is brightened up, after the field is applied. The theory which was put forward first, to explain this phenomenon was due to Voigt[1] who assumed that the movableness of the charges which are responsible for dispersion and which are bound with atoms, depends on the field applied. Next Langevin[2] put forward his theory in which he assumed that the molecules are optically and electrically anisotropic and on application of the field an orientative couple acts on the induced doublet tending to set its axis of easiest polarisability parallel to the field. The temperature agitation acts against this couple and a state of equilibrium is attained in which the axis of easiest polarisability of the molecules favours the direction of the field and hence the medium becomes anisotropic. Langevin's theory did not take into account the influence of permanent moment of the molecules and could not account for the Kerr effect being negative for some polar substances. The general condition was treated expressly with consideration of the permanent moment later on, by Born.[3] Taking into consideration the influence of the permanent moment as well as of the anisotropy of the molecules, the following expression is obtained[4]

$$n_u - n_s = \frac{4\pi\nu}{3} \frac{(n_0+2)^2(\delta+2)^2 E^2}{36n_0} (\theta_1 + \theta_2) = B\lambda E^2$$

So that the Kerr constant B is given by

$$B = \frac{\pi\nu(n_0^2+2)^2(\delta+2)^2}{27n_0} (\theta_1 + \theta_2) \qquad \qquad .. \quad (1)$$

where $\nu =$ number of molecules per unit volume n_p and n_s are the refractive indices for light waves polarised with electric

[1] W. Voigt, Ann. der. Phys., (4), 197. 1901.
[2] P. Langevin, Le Radium, 7, 249, 1910.
[3] M. Born. Ann. der Phys., 55, 177, 1918.
[4] See P. Debye, Marx's Handbuch der Radiologie, Bd. VI, pp. 767 to 768. (The notation has been slightly changed.)

vectors parallel and perpendicular to the field, n_0 is the refractive index in absence of the field, δ is the dielectric constant, E is the applied field, λ is the wave length of the light used

$$\theta_1 = \frac{1}{45 KT} \{(A-B)(A'-B') + (B-C)(B'-C')(C-A)(C'-A')\}$$

$$\theta_2 = \frac{1}{45 K^2 T^2} \{(A-B)(\mu_1^2 - \mu_2^2) + (B-C)(\mu_2^2 - \mu_3^2)$$
$$+ (C-A)(\mu_3^2 - \mu_1^2)\}$$

where A, B, C are the components of polarisability, i.e., the electric moments induced in the molecule along its three principal axes of optical anisotropy due to unit electric field in the light wave, A' B' C' are similar moments induced in the same three directions due to unit electrostatic field, μ_1, μ_2, μ_3 are components of the permanent moment along these directions, K is the Boltzmann constant and T is the absolute temperature.

The value of the Kerr constant can be calculated from equation (1) if θ_1 and θ_2 be known. Recently Raman and Krishnan[1] have carried out the calculation for a few liquids and vapours. The terms involving A', B', C' have been substituted by terms involving A, B, C, obtained from the relation

$$\frac{A'}{A} = \frac{B'}{B} = \frac{C'}{C} = \frac{\epsilon-1}{\epsilon+2} \bigg/ \frac{n_0^2-1}{n_0^2+2}.$$

The terms involving A, B, C have then been evaluated in terms of r the factor of depolarisation of transversely scattered light as obtained from the relation

$$r = \frac{6\{(A-B)^2 + (B-C)^2 + (C-A)^2\}}{10 KT \beta \nu (A+B+C)^2 + 7[(A-B)^2 + (B-C)^2 + (C-A)^2]}$$

where β = the isothermal compressibility.

[1] Prof. C. V. Raman and Mr. K. S. Krishnan, Phil. Mag., Vol. III, Suppl. 713, 1927.

With certain assumptions as regards the form of the molecule and the direction of the permanent moment with respect to the axes of optical anisotropy of the molecules, it has been shown that the values of the Kerr constant thus obtained from equation (1) agree in order of magnitude with the observed values. The ratio of the Kerr constant at two different temperatures for a few fluids has been calculated and the result obtained agrees with the observed values. It has also been shown by them that from equation (1) we can expect also negative values of the Kerr constant and its sign depends on the relative magnitudes of A, B and C. Thus all the observed facts are satisfactorily explained by Born's theory.

It is evident from a glance at the equation (1) as also at the table of Kerr constants in the paper[1] quoted above that the major part of the Kerr constant is contributed by the permanent moment. As for instance, the Kerr constant of non-polar liquids hexane, heptane and octane are. $+1\cdot73$, $+3\cdot26$ and $+4\cdot21$ respectively whereas for Propyl and Butyl alcohol it is -78 and -113 respectively (K for $cs_2=100$). The permanent moment also plays a prominent part in the case of dielectric constant. The contribution to the polarisability due to permanent moment is $\dfrac{\mu^2}{3KT}$ for static field and for a quickly oscillating field of frequency ω,

$$\text{this contribution} = \gamma = \frac{1}{1+2\omega/\omega_o} \quad \frac{\mu^2}{3KT}$$

where ω_0 is the characteristic frequency of the molecules.[2] When ω is small in comparison with ω_0 the polarisability is $\dfrac{\mu^2}{3KT}$ as for static field. As ω approaches ω_0 the real part diminishes and when ω is sufficiently greater than ω_0, γ almost vanishes. The fact that γ is complex shows the presence of

[1] loc. cit.
[2] See P. Debye, Handbuch der Radiologie, Bd. VI, 647.

absorption in this region. The above considerations show that the dielectric constant of polar fields becomes very small for an oscillating field of suitable frequency. This was also experimentally observed long ago for many substances by Drude[1] and others and by S. Mizushima[2] recently in case of alcohols. Considering similarly the influence of permanent moment on the polarisability in case of the Kerr effect also, it is expected that the influence of the permanent moment would vanish for oscillating fields of suitable frequency and similar calculations have been carried out by Tummers[3] in the case of the Kerr constant. As has already been stated, since the major part of the Kerr effect is contributed by the permanent moment the value of the Kerr constant is likely to become very small for oscillating fields of very high frequency.

Again, for some polar substances, the contribution due to the permanent moment is negative and is many times greater than that due to the induced moment, so that for static fields the Kerr constant for such substances is negative, but for quickly oscillating fields it may be expected to fall to zero and finally to attain a very small positive value as the frequency is increased.

Corresponding to the characteristic frequency ω_0 there is a relaxation time T of the molecules given by $\tau = \dfrac{1}{\omega_0} = \dfrac{\rho}{2KT}$

where K is the Boltzmann constant, T is the absolute temperature and ρ is the moment of resistance due to unit velocity of rotation of the molecules. For a spherical molecule of radius a

$$\rho = 8\pi\eta a^3$$

where η is the coefficieut of viscosity. Therefore, the greater the viscosity of a liquid, the greater is its relaxation time.

[1] P. Drude, Zeit Phys. Chemie., 23, 308, 1897.

[2] S. Mizushima, Scient. Papers Inst. Phys. Chem. Research, Vol. V, 201, 1926-27.

[3] J. H. Tummers, Diss. Utrecht, 1914 (quoted by Debye).

Experiments on the relaxation time of the Kerr effect were carried out by Blondlot[1], Abraham and Lemoine[2], James[3], and Gutton[4], who found that there was a relaxation time of Kerr effect of the order of 10^{-9} to 10^{-10} second. Recently however, Beams and Lawrence[5] have shown that the effect observed by the above mentioned authors, instead of being due to difference in the relaxation time of liquids in two Kerr cells, was actually due to difference in the rate of discharge of the Kerr cells which acted as condensers. There is therefore no experimental proof of the existence of a true relaxation time for the Kerr effect.

The Kerr effect for viscous liquids has been studied by the present author for fields of very high frequency and an account of the work is given in this paper.

Technique and Experimental details.

There are various methods of generating short waves but one can get them easily with a valve tube and this method was first tried.
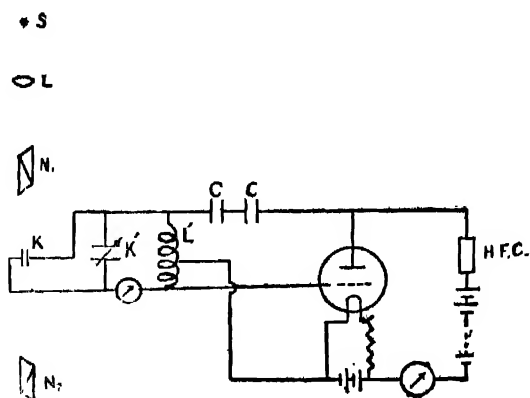
Fig 1.

[1] R. Blondlot, Journ. de Phys., (2) 7, 91, 1888.
[2] H. Abraham and J. Lemoine, Journ. de Phys., (3), 9,262, 1900.
[3] J. James, Ann. de Phys., 15, 954, 1904.
[4] C. Gutton, Journ. de Phys. (5) 2,51, 1912 (5) 3, 206 and 445, 1913.
[5] J. W. Beams and Ernest O. Lawrence, Journ. of the Franklin Inst., 206, 169, 1928.

The arrangement is shown in figure 1. An Osram D.Γ.T. 1 valve was used. A high tension of 600 volts obtained from a battery of Varta cells connected in series with the main was applied to the anode circuit and the oscillating circuit was coupled to it through two Dubilier Mica condensers O O connected in series. A high frequency choke H. F. C was put in the anode circuit. The inductance L, in the oscillating circuit consisted of two to four turns of diameter about 5 cm. for wave lengths from 10 to 40 metres and the variable capacity K′ was a variable air condenser of capacity about ·0001 μF. The Kerr cell was connected parallel to the variable air condenser and a thermomilliameter shunted by a thin copper wire was put in the oscillating circuit as indicated in figure 1. Light from a 1000 c.p. pointolite lamp made parallel by the lens L and polarised at 45° with the horizontal, passed through the Kerr cell K and the emergent light was observed through the analysing nicol N_2. The Kerr cell K was made in the following way. Two brass plates, each 5 cm. long, 8 mm. broad and about 4 mm. thick were fastened to each other with the long faces parallel to each other and were kept insulated from each other by means of two glass strips about 5 cm. long, 1 mm. broad and 1 mm. thick cemented along the edges of the plates with liquid glass, so that there was left, between the plates, an aperture about 1 mm. broad and 6 mm. long through which light could pass. The two plates were further bound together tightly with two pieces of copper wire, mica sheets being used as the insulator between the copper wire and brass plates. Two copper wires soldered to the plates served as leads. The plates thus attached to each other were put in a short glass tube provided with three side tubes, its ends being ground and closed with cover slips cemented with liquid glass. The leads were taken out through the two short side tubes of the glass cell and through the third, liquids could be introduced.

A static field of 300 volts applied to such a cell showed distinct restoration of light in the case of octyl and the higher alcohols. In the case of carbon disulphide or octane, however, no restoration was observed under the said conditions. This shows clearly that for octyl and higher alcohols the Kerr constant is much greater than that for carbon disulphide. Nitrobenzene gave bright restoration with 220 volts across a cell of the above dimensions. The liquids studied for high frequency were octyl, nonyl, decyl and undecyl alcohols. These liquids were treated with freshly ignited quick lime and distilled in vacuum before being introduced in the cell. There was still a little conductivity to the extent that, with a static field of 500 volts across the cell, a current of about ·2 milliampere was obtained. This conductivity has been observed also in case of pure Nitro-benzene by Ilberg[1] and it is evident, as has been pointed out by him, that for quickly oscillating field this conductivity has no effect at all.

The cell was connected parallel to the variable air condenser as shown in Fig. 1 and when the circuit was set in oscillation a very peculiar phenomenon was observed. As soon as the switch in the high tension circuit was put on, the centre of the field of view of the analysing nicol brightened up a little but the effect was immediately masked by two patches of light originating as narrow lines at the surfaces of both the plates and broadening themselves to touch each other at the centre of the field of view. When these patches first appear, they are of reddish tint but they soon become almost white, still retaining a little reddish tinge. The intensity is greater near the surfaces of the plates than at the centre of the field of view. It was also found that on turning the analysing nicol the original bright field of view did not appear, and the liquid appeared to have become translucent. On putting off the switch, the patches disappeared very slowly. The effect

¹ Ilberg Phys. Zeit., 29, 670, 1928.

was practically absent when the capacity of the variable air condenser K′ was a maximum and it was conspicuous when this capacity was very small.

An electrostatic voltmeter of a very low capacity was then constructed as is shown in Fig. 2 and it was calibrated, with the scale at a certain distance, with the help of known static voltage obtained from the Varta battery. This Voltmeter was connected parallel to the Kerr cell and it was observed that
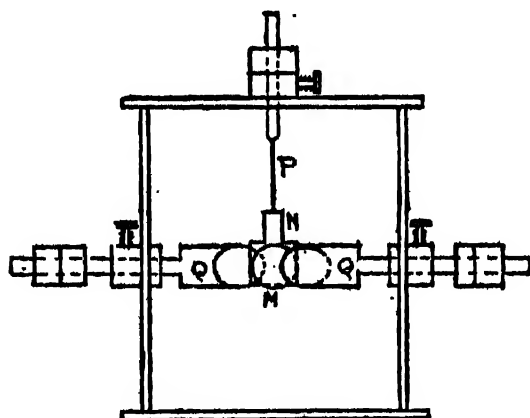
Fig. 2.   P, phosphor bronze strip.
          N, brass plate.
          Q, brass rods.
          M, mirror.

the voltage across the cell depended on the capacity of the variable air condenser K′. This variation was much more conspicuous in case of short waves than in case of waves above 60 metres. It is evident from the above facts that the intensity of this peculiar patch of light depends on the voltage across the cell. Next, different wave lengths were tried and

it was found that for these alcohols, the effect was feeble for wave lengths above 250 metres but it was conspicuous in the region of shorter waves. The effect was found to be absent in the case of static field.

It was suspected that the effect was a spurious one and was due to relative movement of the plates of the Kerr cell caused by the application of the field, but it was observed, that for the same strength of the oscillating field, the intensity of the patch was greater for higher frequency than for longer wave lengths and also careful visual examination could not disclose any relative movement of the plates. Furthermore, there were glass plates between the plates all through their length and they were further bound tightly to each other, so it was not possible for the brass plates of the cell to approach each other and close the slit, after the field was applied. No cement was used with a few other cells but the effect was still observed, unchanged. Some nonpolar liquids like CS_2 and octane were tried but no such effect could be observed. With Nitro-benzene the effect was present but the intensity was much less than that in the case of the higher alcohols. It was evident from these facts that these peculiar patches of light were not due to the Kerr effect but to some other phenomenon.

It has been found by Mizushima[1] that for lower alcohols there is a huge electric absorption over a long range of temperature for a certain wave length of the applied field and also over a long range of frequency of the applied field for a particular temperature. To find out whether there was any such absorption in case of the higher alcohols and also to measure their dielectric constant, Mizushima's method was adopted with slight modification (Fig. 3). A thermo-galvanometer was connected in series with an inductance S, consisting of different number of turns of copper wire for

[1] S. Mizushima, *loc. cit.*

the different wave lengths and a variable plate condenser C.
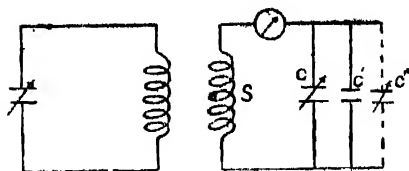
Fig 3

A small capacity C′, placed in a small glass tube sealed at one end was connected parallel to the capacity C. The variable plate condenser C consisted of two brass plates each 3·7 cm. long, 9 mm. broad and about 4 mm. thick, fixed on an ebonite plate with faces parallel to each other so that a glass plate 2·1 mm. thick, 9 mm. wide and about 4·5 cm. long could just slide between the plates. The position of one of the edges of the glass plates could be read on a scale attached to the horizontal face of one of the plates. The circuit was brought to resonance with the oscillating circuit by adjusting the variable capacity C so that the deflection in the thermo-galvanometer was a maximum. A small variable air condenser C″ of capacity about $50\mu\mu$F helped this adjustment. Pure benzene was then introduced into the experimental condenser C′ up to a certain height so that the plates were completely immersed in the liquid and the capacity C was changed till the deflection was again a maximum. The current was observed to be the same as for resonance condition before introducing the liquid, in the case of benzene. The experimental condenser was then carefully dried and the above process was repeated for octyl, nonyl and undecyl alcohols. Undecyl alcohol was studied most carefully and the following results were obtained. The second column represents the ratio of maximum current in the thermo-galvanometer with the liquid to the original maximum current I_0 and this ratio determines the absorption in the liquid.

Undecyl Alcohol.

Wave length in metres.	$\dfrac{I}{I_0}$	$\epsilon.$
70	·80	5·65
47	·71	5·60
30	·66	5·75
6·75	·27	5·90

The above measurements are not very accurate but they show clearly the presence of absorption which increases for shorter wave lengths and also that the influence of frequency on dielectric constant comes in at still shorter wave lengths. For short wave lengths above 6·75 metres, the presence of the observer and the electric absorption affected the impedence of the circuit so that the exact point of resonance could not be determined very accurately, and the value of dielectric constant obtained tended to be a little higher than for longer wave lengths.

The fact that the peculiar patch of light obtained with oscillating field increases in intensity for shorter wave lengths and that the absorption also increases in this region suggests that the said phenomenon has some connection with absorption. It was also observed that the Kerr cell became appreciably heated in a very short time if the circuit was kept oscillating, and this showed that the molecules were still oscillating with the same high frequency as that of the applied field.

As it was not possible to get shorter wave lengths with this arrangement consistently with the cell remaining connected to the circuit, Drude's[1] method of generating short waves was tried. The whole arrangement is shown diagrammetically in Fig. 4. The exciter E. E. consisted of two copper wires each 3 mm. in diameter and from 4 to 8 cm. long for different wave lengths. Each of the wires was provided with a brass ball at one end and was bent in the form of a half circle. Short leads coming out through the walls of the glass

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[1] P. Drude, Wied, Ann. 61. 466, 1897 ; Ann. 8, 336, 1902.

tube were soldered to the other two ends of the exciter as indicated in Fig 4. Kerr cells K of shorter dimensions were made for reducing the capacity. The exciter was mounted on
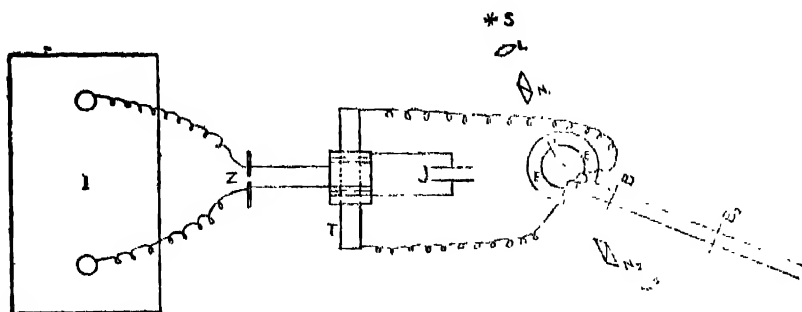
Fig. 4.

an ebonite holder consisting of two long arms attached to a steel spring so that on turning a nut on the guide, one of the arms of the holder would move slowly and the distance between the brass balls could be adjusted in this way. The balls were highly polished and kept dipped in transformer oil. The secondary terminals of a Tesla transformer T were connected to the balls of the exciter. This secondary consisted of about 350 turns of D. S. C. copper wire of No. S. W. G. 24 wound on an ebonite rod of diameter about 6 cm. The primary consisted of 5 turns of insulated thick copper wire wound on a cardboard tube of diameter, about 12 cm. covered with mica sheet. Merely dipping the tube in molten paraffin was found useless. The metal cover of the Leyden jar J was about 15 cm. high, the diameter of the jar being about 8 cm., its walls being about 3 mm. thick. The zinc sparkgap Z was about 4 mm. long. A small induction coil with a mercury break interrupter was used to feed the primary of the Tesla transformer. The secondary system used for measuring the wave length was stretched on an ebonite frame and an ebonite stand. Nickel plated thick wires flattened on one side to slide on the wires of the secondary system was used

as metal bridges. The two straight portions of the secondary system were parallel and at a distance of 2 cm. from each other. A neon tube served as wave-length indicator. With a current of 1·4 amp. in the primary of the induction coil, an orange coloured spark, about 3 cm. long, was obtained at the secondary terminals of the Tesla transformer. The distance between the brass balls, however, when immersed in transformer oil, had to be reduced to ·2 to ·3 mm. in order that the spark could pass and the exciter would begin to generate high frequency oscillations. The position of the first metal bridge B_1 of the secondary system was adjusted till a neon tube held on the exciter at a point between the bridge and the loop of the secondary system would give the maximum glow. A second bridge B_2 was then shifted on the wires till the neon tube held between the two bridges would give the maximum glow. The distance between the bridges gave half the wave length of the oscillation generated in the exciter. With a Kerr cell of which the plates were each 1 cm. long, ·6 cm. wide, and ·82 mm. apart connected to an exciter of diameter of about 5 cm. the wave length of the oscillations generated was found to be 114 cm. When the balls were so much apart that no discharge could pass, and the induction coil was working, a bright restoration was observed in case of all the four alcohols mentioned previously with a cell of dimensions mentioned just now. When, however, the spark was passing, the voltage dropped considerably, and using a nitro-benzene cell, it was observed that intensity of restored light increased with the increase of the spark gap between the balls, but it was very small when this distance was so small that the spark was only visible. The spark gap could not be increased beyond a certain limit as the oscillation ceased to be continuous beyond this limit. Whenever oscillation in the exciter ceased, the direct secondary of the Tesla transformer was connected to the Kerr cell and so the field of view brightened very much at the instants at which the oscillations

ceased. By suitably adjusting the distance between the discharge balls, much fainter and almost steady restoration of light was observed, and though its intensity fluctuated a little due to fluctuation of the current in the primary of the Tesla transformer, it could not be confused with the bright restoration due to E.M.F. at the secondary terminals of the transformer. With one of the exciters the wave length generated was about 156 cm. The wave length depended practically on the dimensions of the Kerr cell. With very short cells shorter wave lengths could be obtained but that would diminish the intensity of the restored light. At 156 cm. restoration was observed with all the alcohols. At 114 cm. however, it was clearly absent in case of undecyl alcohol. The intensity of restored light was so faint that with this arrangement it was not possible to determine at which wave length the Kerr effect began to diminish. For still longer wave lengths up to 4 metres, along with restoration the peculiar phenomenon mentioned previously was present but it was very feeble. It was absent with E.M.F. direct from secondary of the Tesla transformer. When, however, for undecyl alcohol, the Kerr effect was absent at about 114 cm. this phenomenon also almost vanished. Shorter wave lengths were required for getting the disappearance of Kerr effect for octyl and nonyl alcohols but it appeared that the arrangement had to be slightly modified for observing the phenomenon more conveniently. The work is being followed up and an account of further investigations will be published very shortly.

Discussion.

The disappearance of Kerr effect for undecyl alcohol is quite concordant with dielectric constant measurements. We see from Landolt and Bornstein table that the influence of frequency begins in the case of heptyl alchol, at wave lengths between 91 cm. and 75 cm. and for octyl alcohol, even with 91

cm. the dielectric constant is only $3 \cdot 4$, being much less than the dielectric constant of undecyl alcohol for higher wave lengths though this undecyl alcohol has certainly smaller dielectric constant than octyl alcohol for longer wave length. It is therefore expected from foregoing considerations that the influence of frequency must be very great in case of undecyl alcohol for 114 cm. From this fact we get an idea of the time of relaxation of the Kerr effect for these higher alcohols. Though it is not very accurately determined by the above investigatations, it is certain that this time of relaxation lies between 10^{-8}sec. and 10^{-9}sec.

The peculiar patch of light appearing with long waves mentioned previously is some phenomenon other than the Kerr effect. The facts that the liquid appears to be translucent and that there is electric absorption when this phenomenon is most conspicuous suggest that it may be some kind of scattering. A theoretical discussion on this point with some remarks on Bramley's [1] recent work is reserved for a separate paper.

The author's grateful thanks are due to Prof. C. V. Raman, F.R.S., for kindly suggesting the problem, and taking keen interest during the progress of the work.

Arthur Bramley, Journ. Franklin Inst., 206, 151, 1928.

A study of the electric glow discharge through air by an interferometric arrangement.

By

J. B. Seth, M.A. (Cantab.), Chetan Anand, M.A. (Punjab) and Bal Mukand, M.Sc. (Punjab).

The interference fringes used in these experiments were produced by Jamin's plates. One of the beams of light was passed through a tube containing three side tubes, the two end ones having platinum wires sealed in for the purpose of causing the glow discharge, and the middle one being used for varying the pressure of the air inside. The second beam was also passed through a similar tube which could be connected to the experimental tube and exhausted, so that the two paths of light would be kept exactly similar, except for the passage of discharge through one of them. An ordinary open-end mercury manometer was used to measure the pressure of the air inside the tubes, with the help of the known atmospheric pressure.

With such an arrangement, using a monochromatic (sodium) light, or using white light from a pointolite lamp and observing the fringes in the spectrum produced by a grating spectrometer, a very curious and, so far as we know, hitherto unrecorded phenomenon is observed. At the starting of the discharge in the ordinary way by means of an induction coil, there is a sudden shift of the fringe system, indicating a decrease in the refractive index of the air in the experimental tube.[1] During the time that the discharge is passing, the shift remains constant, i. e., the fringe system stays in

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[1] A tentative announcement of this was made in the "Nature" of Dec. 17th, 1927.

its shifted position but at the instant of discontinuation of the discharge, there is an equal and sudden shift back of the fringes into their original position. The amount of the shift is dependent on the voltage applied to produce the discharge and on the pressure of the air inside the tubes. For a fixed value of the applied e. m. f. the amount of shift varies with the pressure and becomes a maximum for a certain value of the pressure which is different for different voltages. This is clearly shown in the graphs given in Fig. 1., which represents three sets of observations with three voltages, the lowest curve being for the lowest voltage. The amount of shift in terms of a fringe width could easily be estimated by mere inspection as the fringes used were fairly wide and of good visibility. It can also be accurately determined by means of a low power microscope having a glass scale in its eyepiece and which replaces the eyepiece of the observing telescope. The amount of the shift depends on the applied voltage and can be made quite large, even up to several fringes. When, however, the shift is much more than one-fringe width, it becomes difficult to judge its amount on account of its suddenness.

Fig. 1.
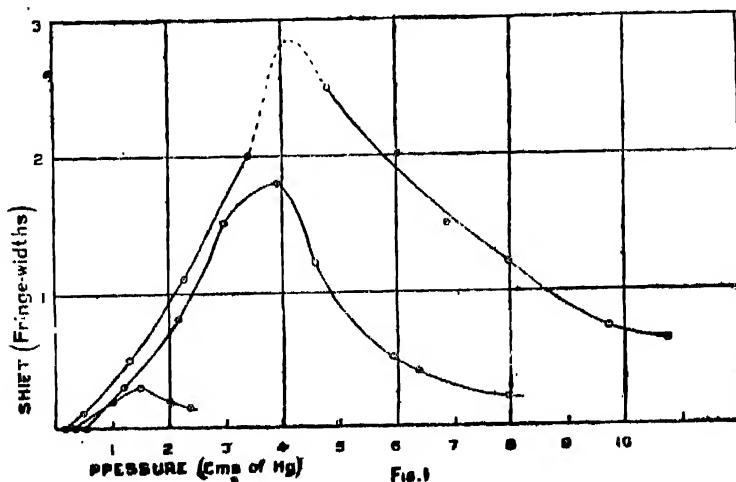
Another characteristic of the shift is that it is maximum for that portion of the tube where the discharge is actually

passing and decreases as we go away from the region of the discharge. As a consequence, the fringes (which should be straight linear) not only suffer a sudden shift but also become curved, the maximum bulge being at the central portion of the system which corresponds to the region of the discharge, which at the time of the maximum shift is in the form of a tubular band and not occupying the whole width of the tube. The amount of the shift for various portions of the tube can also be measured separately by moving a narrow slit across the path of the beam of light passing through the experimental tube and thus observing only a limited portion of the field. Such a measurement shows that the sudden shift gradually decreases as we go to the sides.

The fact that the shift appears suddenly and disappears equally suddenly regardless of the time for which the discharge has been passing, indicates that this is not due to any general increase of temperature brought about by the passage of the discharge. Moreover, such an increase of temperature should make the fringes move in the opposite direction, for the conditions being more or less of constant volume, the increase in temperature would cause increase in pressure and therefore increase in refractive index. The sudden shift, however, is in the direction indicating decrease of refractive index. The above-mentioned curvature of the fringes also remains constant which also indicates that the observed effect is not due to a general increase of temperature.

It was therefore at first concluded that the shift we were observing, was due to an increase in the velocity of light in the air brought about by the intense ionisation produced when the glow discharge is passing through it, and that the shift becomes a maximum when the ionisation is maximum, which would be so when the current density of the discharge is maximum. To ascertain this, the current density was obtained by noting the amount of total current flowing through the tube by including a milli-ammeter in series with the tube and the induction coil

and also determining the diameter of the discharge glow through the tube. As shown in Table I, it turned out that the shift was maximum when the current density was maximum.

These experiments were really started to test whether ionisation of a gas has any effect on the velocity of light through it. To begin with, the ionisation was produced by coating the inside of the tube with a uranium salt and the refractive index of air found in the ordinary manner first when the beam of light passed through an ordinary tube and then through this prepared tube. No change of refractive index was of course noticed. Next, one of the two tubes placed between the Jamin plates was surrounded by thick lead cloth and both exposed to X-Rays from a Coolidge tube. No shift of fringes was observed in this case either. But as soon as we passed the glow discharge through one of the tubes, the shift was observed. It must be mentioned here that the elctrodeless discharge from a Tesla coil produces no such effect.

We were strengthened in our conclusion that the shift was due to a change of refractive index of air on account of ionisation, from the result of similar experiments on helium by

TABLE I.

Pressure in the tubes cms. of Hg.	Sudden shift in terms of a fringe width.	Sudden change in pressure mms. of Hg.	Current milliamperes.	Diameter of discharge cm.	Current density milliamperes.
0·50	0	0	3·8	1·30	2·86
1·30	·6	·8	2·2	·70	5·7
1·50	·8	1·0	2·0	·50	10·2
1·83	1·0	1·2	1·7	·40	13·5
2·30	1·2	1·6	1·4	·30	19·8
3·00	1·5	2·0	1·4	·25	28·5
3·34	1·7	2·4	1·1	·20	35·0
3·94	1·5	2·0	·6	·20	19·1
4·94	·4	·5	·02	·15	1·13
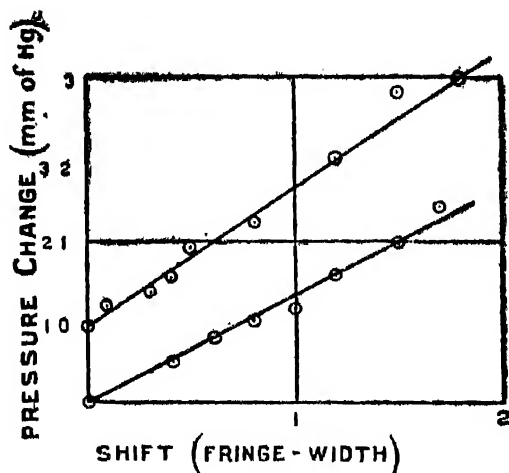
FIG. 2

Mc.Gurdy and Branley.[1] There is one essential difference however, between their observations and ours. They noticed the shift in one direction or the other or no shift at all according to the wave length of the light they used. Our observations show shift for all wave lengths and in the same direction ; the amount of shift being greater in the blue than in the red region of spectrum. Therefore, the cause of the shift in the two cases must be different. Moreover, according to Larmour,[2] the change in velocity of light due to ionisation would be too small to be observed for small wave lengths. We therefore had to look elsewhere for the cause of our shift ; and this was apparently provided when the behaviour of the manometer was observed. It was seen that as soon as the discharge was started, the Hg. column was depressed showing a sudden increase of pressure in the apparatus. On stopping the discharge, the mercury came back to its original level. The curve between the sudden shift is straight linear. See Fig. 2, also Table I.

A general increase of pressure inside the tube would however, cause the motion of the fringes in the opposite

[1] Phys., Rev., March, 1926, p. 314.
[2] Electrician, Jan. 9th, 1925, also Nature, Jan. 24th, 1925.

direction to that observed for the sudden shift, and therefore the inference we draw from the above observation is that the portion of the air through which the discharge is actually passing is attended with a rarifaction, that air is suddenly pushed away from this region, so that there is a gradient of pressure established between it and the mano-metre. This inference is strengthened by observing the sudden shift when the experimental tube is isolated from the auxi-liary tube and the manometer. In this case, the amount of sudden shift is reduced to nearly a half of its previous value. Again, if a fairly large volumed vessel is included in the arrangement, the sudden shift remains the same as before but the sudden increase in pressure is diminished. Also, if the beam of light is allowed to pass through the periphery of the tube, so that it does not traverse the region of the glow discharge, and the tube is isolated, then at the time of the start of the discharge there is a slight *kick* of the fringes in the direction opposite to the sudden shift.

It may be mentioned in conclusion that by replacing the above discharge tube with another, through the centre of which was stretched a thin nicrome wire, through which a current could be passed to make it glow, it was observed that to begin with there is a shift (but not too sudden) of the fringes in the direction of the sudden shift, showing a decrease of refractive index, and this is followed by shift in the opposite direction showing general increase of tempera-ture and therefore of the pressure and the refractive index. In the case of the glow discharge there is no gradual shift of fringes in the direction of increase of refractive index.

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Thermo-E.M.F. generated in a copper wire subjected to asymmetric heating and longitudinal tension.

By

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A thermo-e. m. f. is generated in a circuit consisting of a single wire when the same is subjected to asymmetric heating —see Benedics, C. R. 165, September, 1917, p. 391. His experiments showed that in a homogeneous matter unequally heated, an electric current is generated which varies as the difference of temperature between the two portions of the conductor.   Such an e.m.f. seems to become more pronounced if the material experimented on is under strain. Thus, thermo-electric effect in a homogeneous wire with abrupt changes of cross section has been demonstrated by L. Pechinger.[1] Reference may also be made to the work of J. M. Benade,[2] who found thermo-e.m.f.'s produced by maintenance of a steep temperature gradient along a constriction The work of the latter definitely precludes the phenomenon being due to inverse Thomson effect.

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[1] Akad. Wiss. Wien. Ber. 131. 2a, No. 8, 1922, p. 491. Noticed in Science Abstracts, 1924, No. 687.

[2] Phys. Rev. 18, p 199, September, 1921.

The present experiment was undertaken to test the effect in the case of a circuit made up of one uniform metal (a copper wire in the present case), subjected to asymmetric heating when one portion of it was also subjected to a strain caused by stretching it within and beyond the elastic limit right up to the breaking point.

The apparatus consists of a simple arrangement represented in the accompanying diagram, Fig. 1, which explains itself. The lower piece of ebonite was connected to a permanently fixed hooked iron rod. The upper ebonite piece was connected by means of another iron rod to the screw arrangement at the top, the rotation of which produced the required stretching. The portions of the wire at A and B passing through the ebonite pieces were so arranged that the wire could not slip through the holes in these pieces. There were a number of coils in the parallel portion of the wire the length of which was much longer than AB, and which was held loose between C and D. Thus the effect of stretching was limited to elongate the portion AB only. The increase in the distance between the two ebonite pieces resulted only in uncoiling the unstretched portion CD. Care was taken that the copper wire did not touch any conducting material anywhere except of course at the galvanometer terminals.

The amount of stretching produced was observed by means of a cathetometer placed at a distance and near the scale on which the deflections of the galvanometer were read. For every stretching produced, the portion of the edges X and

Y of the ebonite pieces were both read to eliminate any errors due to the raising of the lower piece.
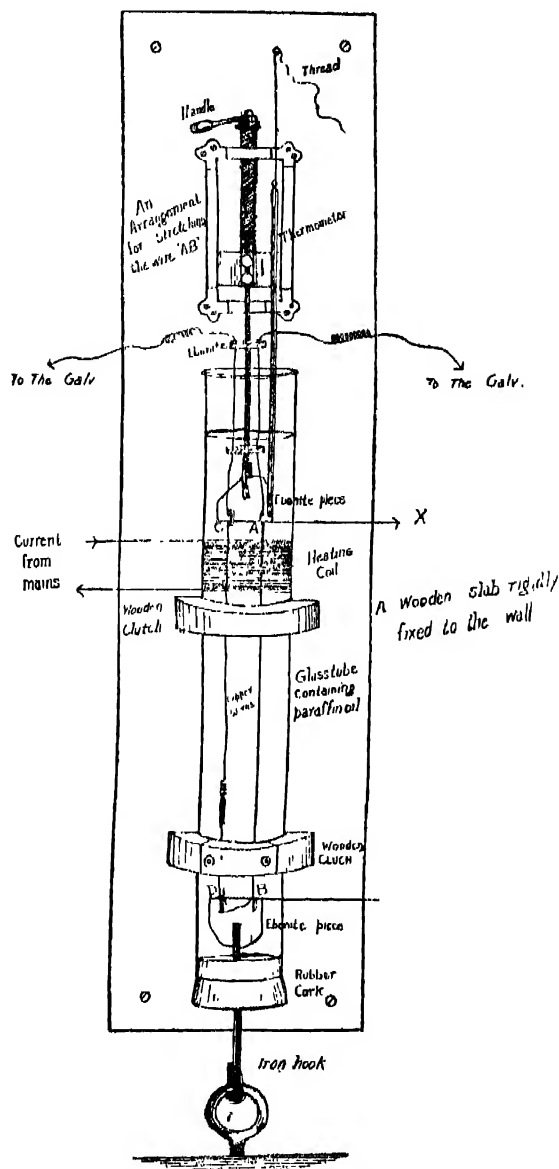
Diagramatic Representation of the Apparatus

FIG. 1.

The heating of only one, the upper, portion of the wire was effected in the way shown in Fig. 1. The tube was kept nearly full of paraffin oil. A stirrer (not shown in the figure)

was used to keep the temperature of the upper portion uniform. The temperatures of the upper and lower portions of the oil bath were registered by two thermometers kept hanging inside the tube and which could be placed at different levels by manipulating the suspending thread. The lower thermometer is not shown in the figure. It was found that the temperature of the lower portion of the bath below the heating coil did not rise but remained at the room temperature.

The e.m.f.'s generated were shown by the deflections of a sensitive galvanometer. The most sensitive galvanometer available in the laboratory was of the moving-magnet type which was rather troublesome and necessitated working at night or at such times as other people were not working, setting up stray magnetic fields. All the same, there was a slight change in the zero of the galvanometer taking place all the time which could not be got rid of, and to eliminate the error due to this, the readings of the zero position were taken immediately before and after any deflections produced and the mean of the two positions taken as the correct zero. The resistance of the galvanometer was about 10 ohms and its time period kept at about 10 seconds. The scale on which the deflections were read was at a distance of 296 cms. from the mirror of the galvanometer. It was calibrated with the help of a micro-ammeter which showed that a deflection of 1 cm. on the scale, corresponded to a current of 0·027 micro-ampere. Knowing the total resistance of the circuit (10·85 ohms), this means an e.m.f. of 0·29 or approximately 0·3 microvolt per cm. deflection.

It can be easily shown that the change in the resistance of the copper wire due to stretching and heating are negligibly small so that the deflections of the galvanometer can be taken to represent the e.m.f.'s actually generated.

The results of various observations can be summarised as follows. The generated e.m.f. increases with the temperature difference between the two portions of the wire and the

increase is more marked, the greater the stretching force. This is clearly shown in the curves shown in Fig. 2.

Fig. 2
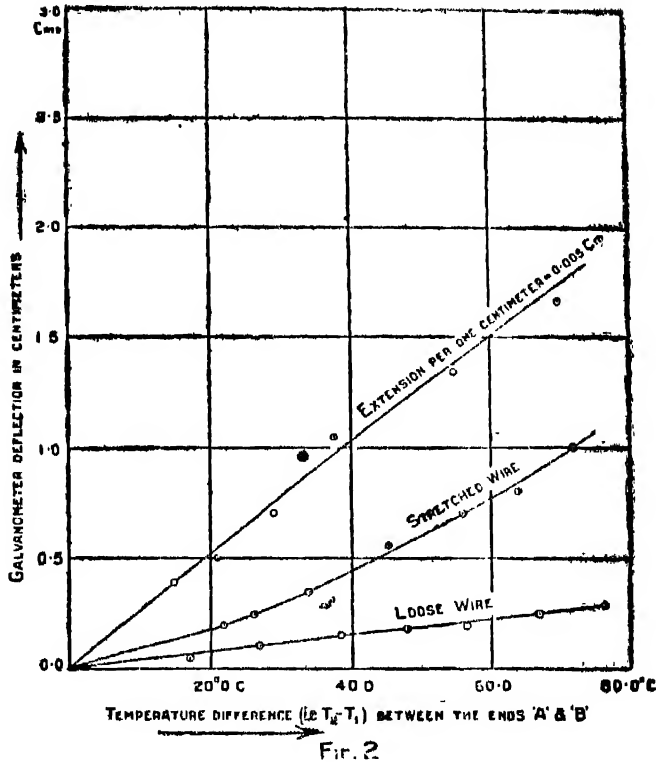
A series of observations were taken in which the extension was kept constant, the temperature of the upper portion of the bath raised and then allowed to fall, keeping the lower temperature constant. Deflections of the galvanometer for various temperature differences were taken. This was repeated for various extensions produced. From these observations, curves showing the deflections for different extensions but constant difference of temperature were plotted, a few of which are shown in Fig. 3. The lowest of these curves, namely for $T_2 - T_1 = 0$, was obtained directly by keeping the temperature of the bath uniform throughout at the room temperature, and noting the galvanometer deflections for various extensions.

The curves in Fig. 3 are all similar, showing that as the extension is increased, the e.m.f. produced rises to a maximum
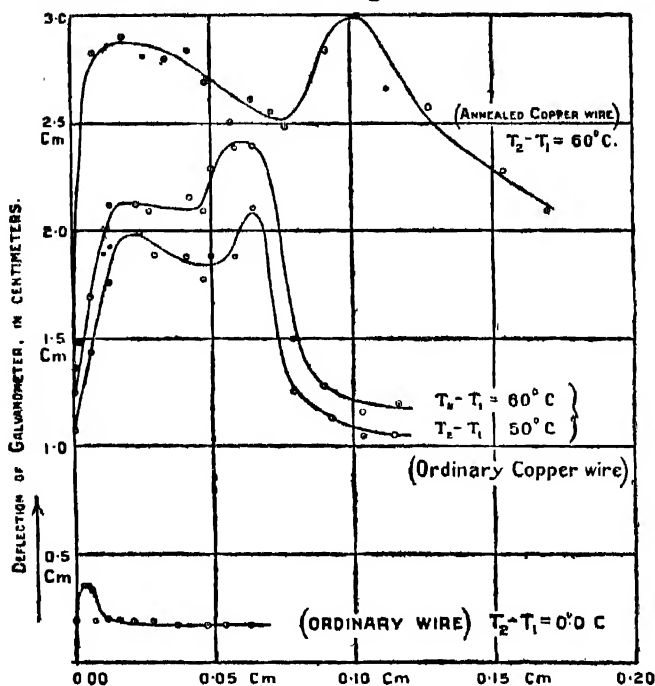
FIG. 3

and then to a second maximum before attaining a constant value. They also resemble the stress-strain curves for a loaded wire as given in text books such as Poynting and Thomson's "Properties of Matter," p. 54. The first maximum in the curve corresponds approximately to the stage when the yield point is attained. After this, the wire gets in a semi-plastic condition and during this state, the e.m.f. rises to a maximum once again, falling to a nearly constant value before the breaking point is reached. There seems to be no doubt that the e.m.f.'s generated in the wire and observed here, are intimately connected with the breaking up of the aggregates of the crystals in the material of the wire which produces permanent set in it, and that the asymmetric heating is necessary to bring about the changes in the motion of the electrons which are responsible for these thermo-e.m.f.'s.

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On the Spectra of As III and Sb III

BY

P. PATTABHIRAMIAH, M.A., AND A. S. RAO

In two previous papers [1] on the first spark spectra of *Ge* and *Sn* Narayan and Rao reported a number of doublets which were believed to be the chief members of the doublet system characterising the second spark spectra of *As* and *Sb*. The present paper deals with the analysis of the spectra due to the doubly ionised *As* and *Sb*. From the position of these elements in the periodic table, it would be expected that their spectra consist of doublet and quartet terms and that their structure resembles that of the first spark spectra of *Ge* and *Sn*. These have been almost completely analysed by Narayan and Rao and in each case the deepest term was found to be of the ^2P type. The structure diagrams of doubly ionised *As* and *Sb* may be written down as,

As. K
   2

L_1 L_2
2   6

M_1 M_2 M_3
2   6   10

N_1 N_2 N_3 N_4
2   1

O_1 O_2 ...

[1] Rao and Narayan, Proc. Roy. Soc., 119, 607 (1928)
Narayan and Rao, Zeit. fur. Phys., 45, 350 (1927)

Sb. K.
     2

       L$_1$ L$_2$
       2   6

           M$_1$ M$_2$ M$_3$
           2   6   10

                N$_1$ N$_2$ N$_3$
                2   6   10

                    O$_1$ O$_2$ O$_3$
                    2   1

                    P$_1$ P$_2$

In atoms of this type only one electron normally is in an uncompleted 'shell,' all the remaining underlying 'shells' being complete and consequently spectrally neutral. The transitions of this electron determine the chief low-lying terms in the spectra.

The regular terms 1^2P, 1^2S, 1^2D, 1^2F, etc., and their Rydberg sequences arise when this outermost 'P' electron is shifted successively through the various 'shells.' But when one of the 's' electrons is excited new groups of terms would be found which are also characteristic of the spectra.

The configuration,

$$s^1p^2 \text{ gives } {}^4\overline{P}, a^2D, a^2\overline{P}, a^2S$$
$$s^1p^1s^1 \text{ gives } b^2P, b^4P \qquad \text{and so on.}$$

The analysis of these spark spectra showed the existence of all the regular doublet terms of 's^2p_1' configuration and probably a^2D and $^2\overline{P}$ of 's^1p_2' configuration.

Most of the lines which have entered into the present classification have been previously recorded. The existing

measures included those of Eder and Valenta, Exner and Haschek, and Herpertz upto $\lambda 2300\text{Å}$ and those of Bloch beyond $\lambda 2200\text{Å}$ in the case of Arsenic; and in the case of Antimony, in addition to the measurements of E and V and Ex and H the recent measurements of Schippers are available, upto $\lambda 2100\text{Å}$ while beyond $\lambda 2100\text{Å}$ the measurements of Bloch Mce Lennan, Young and Ireton are available. In the analysis of the spectrum of Sb the investigation of Kimura and Nakamura who have studied the cathode spectrum of the element under different conditions of excitation was of great use and it may be observed that with the exception of a few, all the lines observed by these authors as belonging to $Sb\ III$ have entered into the present classification.

In connection with this work to provide information regarding the nature and behaviour of the various lines and to help in assigning the lines to the different stages of ionisation, photographs of the spark spectra of the two metals have been taken as usual under a variety of experimental conditions. In the case of As, in addition to the usual methods, discharge through the vapour of Arsenic-trichloride was also examined. These photographs together with the application of the relativity Regular and Irregular doublet laws through the sequence $Ga\ I$, $Ge\ II$, and $As\ III$, and $In\ I$, $Sn\ II$ and $Sb\ III$, made the present analysis possible. From observations of the spark spectra of Sb in the visible region if was felt that the strong pair $\lambda\lambda 6246\cdot9$ and $6287\cdot8$ in the red must clearly be the diffuse pair. These lines are intense under maximum excitation and are easily suppressed by self-induction. This together with the diffuse nature of the pair led to the identificationof the inverted diffuse $1D$, $2P$.

Tables I and II show the relativity doublet law variations in Ga-like and In-like atoms. Tables III and IV give the lines classified together with their designation and the term values obtained. Tables V and VI show a comparison of the term-values in Ga-like and In-like atoms.

As in *Ge II* and *Sn II* the '*x*' term is of the nature of '*D*.' These terms arising from similar electron configuration show a regular variation in passing through the sequence *Ga* I, *Ge* II and *As* III and *In* I, *Sn* II, *Sb* III. The ^2x, ^2F combination which should be intense falls in *Sb III* at ν, 60143. In Bloch's data there is a pair $\nu\nu$59591·2 and 58411·2 with $\triangle\nu$=1180. This confirms probably the $x_{2,3}$ separation.

Other combinations involving the characteristic difference 722 in *As* and 1668 in *Sb* are given in Table VII. In the case of Arsenic $^2\overline{P}, 2^2P$ appears to be most probable.

TABLE I.

	$1^2S_1 - 2^2P_1$	Diff.	$1^2S_1 - 2^2P_2$	Diff.	$2^2P_1 - 2^2P_2$ $\triangle\nu$
Ga I	[8266]		[8374]		[108]
Ge II	16604	8338	16963	8589	359·6
As III	24764	8160	25487	8524	723·2

TABLE II.

	$1^2S_1 - 2^2P_1$	Diff.	$1^2S_1 - 2^2P_2$	Diff.	$2^2P_1 - 2^2P_2$ $\triangle\nu$
In I	[7484]		[7776]		[292]
Sn II	14607	7123	15493	7717	886·1
Sb III	21772	7165	23440	7947	1668·2

TABLE III.

As. III.

Classification.	λ I	ν (vac)	△ν	Term.	Values.	Effective Quant. No.
$1^2P_1 - 1^2S_1$	974·62 (8)	102604		1^2P_1	220221	2·1172
$1^2P_2 - 1^2S_1$	1008·43 (7)	99658	2946	1^2P_2	217275	2·1314
$1^2S_1 - 2^2P_1$	4037·17 (8)	24763·8		X	120281	2·8647
$1^2S_1 - 2^2P_2$	3922·61 (10)	25487·0	723·2	1^2S_1	117617	2·8969
$2^2P_2 - 2^2S_1$	3255·69 (5)	30708·0		1^2D_2	110439	2·9897
$2^2P_1 - 2^2S_1$	3180·78 (5)	31431·25	723·25	1^2D_3	110083	2·9944
$1^2D_2 - 2^2P_2$	5460·80 (1)	18308·0		$1^2\overline{P}_1$	106280	3·0511
$1^2D_3 - 2^2P_2$	5568·42 (4)	17954·1	353·9	$1^2\overline{P}_2$	104793	3·0744
$1^2D_2 - 2^2P_1$	5684·97 (7)	17586·1	721·9	2^2P_1	92853	3·2605
$X - 2^2P_1$	3645·08 (4)	27427·6		2^2P_2	92129	3·2734
$X - 2^2P_2$	3851·80 (5)	28147·9	720·3	1^2F	63975	3·9281
$2^2P_2 - 2^2D_2$	2989·54 (4)	33441·9		2^2S_1	62145	3·9854
$2^2P_2 - 2^2D_3$	2982·00 (10)	33526·5	84·6	2^2D_2	58689	4·1011
$2^2P_1 - 2^2D_2$	2926·32 (10)	34164·4	722·5	2^2D_3	58603	4·1043
$2^2D_2 - 4^2P_2$	3572·94 (3)	27981·4		3^2P_1	52296	4·3445
$2^2D_3 - 4^2P_2$	3583·79 (5)	27896·5	84·9	3^2P_2	51994	4·3572
$2^2D_2 - 4^2P_1$	3591·40 (2)	27837·5	143·9	2^2F	40418	4·9418
$2^2D_2 - 2^2F$	5471·95 (6)	18270·7				
$2^2D_3 - 2^2F$	5497·12 (6)	18187·0	83·7	1^2G	[39600]	4·9927
$2^2P_2 - 3^2D_2$	...	[57122]		3^2D_2	35009	5·3099
$2^2P_2 - 3^2D_3$	1749·7 (8)	57153	31	3^2D_3	34978	5·3110
$2^2P_1 - 3^2D_2$	1728·8 (1)	57843·6	721·6	4^2P_1	30851	5·6564
$1^2F - 1^2G$	4101·49 (6)	24375·4	...	4^2P_2	30707	5·6696
$1^2D_2 - 1^2F$	2152·18 (4)	46464		4^2D_2	23926	6·4237
$1^2D_3 - 1^2F$	2168·83 (3)	46108	356	4^2D_3	23908	6·4261
$3^2P_2 - 3^2D_2$	5885·67 (1)	16986·3		4^2S_1	23242	6·5175
$3^2P_2 - 3^2D_3$	5875·56 (2)	17015·6	29·3			
$3^2P_1 - 3^2D_2$	5783·48 (6)	17286·5	300·2			

Classification.	λ	I	ν (vac)	Δν
$3^2P_2 - 4^2S_1$	3477·02	(2)	28753·3	
$3^2P_1 - 4^2S_1$	3441·09	(2)	29053·5	300·2
$3^2P_2 - 4^2D_2$	...		[28070.]	
$3^2P_2 - 4^2D_3$	3559·43	(1)	28087·6	17·6
$3^2P_1 - 4^2D_2$	3523·98	(1)	28370·1	300 1
$1^2P_1 - 1^2P_1$	877·65	(9)	113941	
$1^2P_1 - 1^2P_2$	866·31	(10)	115428	1487
$1^2P_2 - 1^2P_1$	900·90	(9)	111000	2941
$1^2P_2 - 1^2\bar{P}_2$	889·05	(10)	112480	1480
$1^2P_1 - 1^2D_2$	910·90	(5)	109782 (obs)	2948
			109782 (cal)	
$1^2P_2 - 1^2D_3$	932·90	(3)	107193 (obs)	
			107192 (cal)	
$1^2P_1 - X$	1000·56	(7)	99944 (obs)	
			99940 (cal)	2945
$1^2P_2 - X$	1030·93	(5)	96999 (obs)	
			96994 (cal)	

* The wave-length measurements in the vacuum grating region, used in this work, are from the unpublished work of R. A. Sawyer of the University of Michigan to whom the grateful thanks of the authors are due for permitting them to use the data.

TABLE IV.

Sb. III.

Classification.	λ	I	ν	Δν		Term.	Term value.	Eff. Quant. Number.
1S−2P₁	4591·89	8	21771·4			1S	107456·1	3·0309
1S−2P₂	4265·09	10	23439·6	1668·2				
						2P₁	85683·1	3·3942
2P₂−2S	4693·09	8	21302·0			2P₂	84016·5	3·4277
2P₁−2S	4352·25	10	22970·2	1668·2				
						2S	62714·5	3·9678
2P₂−2D₂	...		[28288·9]	237·6				
2P₂−2D₃	3504·51	10	28526·54			2D₂	55726	4·2087
2P₁−2D₂	3337·15	9	29957·11	1668·21		2D₂	55490	4·2181
2D₃−3F	3683·469	4	27140·6			3F	[28350]	5·9007
2D₂−3F	3651·704	2	27376·71	236·11				
2P₂−3S	2270·13	3	44036·68			3S	39978·5	4·9687
2P₁−3S	2182·5	1	45704·6	1668·08				
1S−3P₁	1839·1	4	54374·4			3P₁	53082·1	4·3123
1S−3P₂	1814·3	2	55117·7	743·3		3P₂	52338·1	4·3426
2S−4P₁	3914·4	2	25540·47			4P₁	37174·0	5·1531
2S−4P₂	3850·6	4	25965·28	575·19		4P₂	36749·2	5·1828
3P₁−4S	4245·34	1	23548·68			4S	29538·1	5·7812
3P₂−4S	4384·04	1	22803·74	744·94				
x₂−2P₂	2482·84	1	40264·3			x₂	124280·8	2·8182
x₃−2P₃	2557·60	3	39087·4	1176·9		x₃	123103·9	2·8313
x₃−2P₁	2590·24	4	38594·9	1669·4				
1D₂−2P₂	5691·0	1	17567·9			1D₂	101584·4	3·1172
1D₃−2P₂	6246·9	4	16004·06	1563·84		1D₃	100021·1	3·1415
1D₂−2P₁	6287·8	3	15899·96	1667·94				
1D₃−1F	2669·64	6	37447·09			1F	64187·3	3·9281
1D₃−1F	2786·02	8	35882·9	1564·19				

TABLE V.

Element.	2^3P_1	3^2P_1	1^2S_1	2^2S_1	1^2D_3	2^2D_2	3^2D_2	1^2F
Ga I	[15326]	...	23592	10795	13592	7569	...	...
Ge II	12408	...	16559	8464	11906	7127	15906	[7080]
As III	10317	...	13069	6905	12232	6511	13365	7108

TABLE VI.

Element.	2^2P_1	3^2P_1	1^2S_1	2^2S_1	1^2D_1	2^2D_2	3^2D_2	1^2F
In I	14811	7806	22295	10366	13752	7570	...	...
Sn II	11540	...	15192	...	11410	6826	14712	7100
Sb III	9520	5898	11939	6968	11113	6164	13809	7126

TABLE VII.

Unclassified Pairs.

Element.	λ	I	ν	$\triangle\nu$	Probable classification.
As	3688·83		27474·7		
	3545·75		28195·9	721·2	$3^2\overline{P}_2, 2^2P$
	3319·39		30118·7		
	3241·46		30842·7	724·0	$3^2\overline{P}_1, 2^2P$
	3109·1		32156·5		
	3040·79		32878·0	721·5	
Sb	4245·34		23548·68		
	3378·91		25215·18	1666·5	$3^2\overline{P}_1, 2^2P$
	3739·5		26730·76		
	3520·11		28400·12	1669·36	
	2617·63		38195·63		
	2507·83		39863·8	1668·17	
	5178·06		19306·9		
	4766·19		20975·27	1668·37	$3^2\overline{P}_2, 2^2P$

On the Spectrum of Doubly Ionised Clhorine.

BY

K. Majumdar and S. C. Deb.

Abstract.

Thirty lines of Cl III are classified in addition to those previously classified by Bowen. These have been attributed as arising from the transition $2M_2(M_3 \leftarrow N_2 \leftarrow N_3)$.

The spectrum of doubly ionised chlorine has been analysed by Bowen,[1] but the analysis is yet incomplete. Bowen[1] has classified eighty-eight lines, of which about thirty are in the Schumann region. In the present paper an extension has been made over the previous analysis.

The structure diagram of Cl III will be similar to those of S II and P I and following Prof. Saha's[2] scheme may be written as follows :—

$$
\begin{array}{ccccc}
K_1 & & & & \\
2 & & & & \\
& L_1 & I_2 & & \\
& 2 & 6 & & \\
& & M_1 & M_2 & M_3 \\
& & 2 & 3 & \\
& & N_1 & N_2 & N_3 \\
& & & O_1 & O_2 & O_3
\end{array}
$$
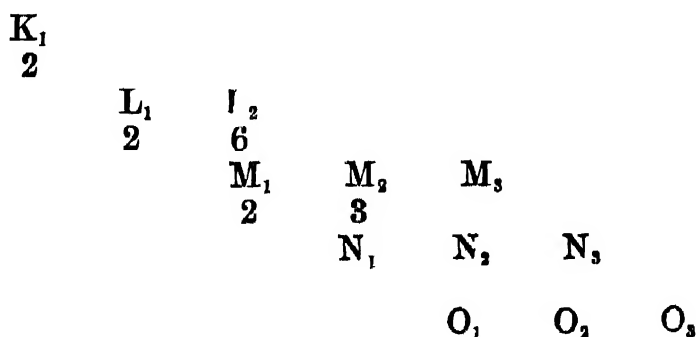
Thus, the most important transitions will be

$$
3M_2 \begin{array}{c} \nearrow 2M_2M_3 \searrow \\ \\ \searrow 2M_2N_1 \nearrow \end{array} 2M_2N_2 \begin{array}{c} \nearrow 2M_2N_3 \\ \\ \searrow 2M_2O_1 \end{array}
$$
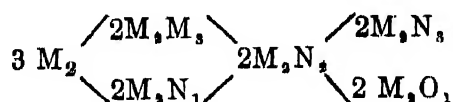
Bowen has obtained the lines, though not completely, corresponding to all the above transitions, excepting the transition $2M_2M_3 \leftarrow 2M_2N_2$. Some of the lines due to this

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[1] Bowen, Phys. Rev., 31, 35 (1928).

[2] Saha, Phil. Mag., 3, 1365 (1927)

transition have been found and are collected in Table I. In addition, we have obtained some more combinations due to the transition $2M_2N_2 \longleftarrow 2M_2N_3$, which are shown in Table II. The combinations obtained here include only the quartet terms, the new terms obtained being ⁴P₁, ⁴P₂, ⁴P₃ due to $2M_2M_3$ and ⁴F₂, ⁴F₃, ⁴F₄, ⁴F₅ and ⁴D₁ due to $2M_2N_3$. No inter-combinations have so far been obtained in any of the transitions.

The lines are from the data given by Block,[3] who has, by varying the stimulus by electrodeless discharge method, separated the lines of chlorine due to different stages of ionisation.

TABLE I.

$2M_2(M_3 \longleftarrow N_2)$.

²M₂M₃ / 2M₂N₂	⁴P₁ 118·1	⁴P₂ 168·1	⁴P₃
⁴D₁ 258·6	(1) 21291·8	—	
⁴D₂ 433·1	—	(3) 21668·7	—
⁴D₃ 602·5		(5) 22101·2	(2) 22269·4
⁴D₄			(3) 22872·1
⁴P₁ 102·4	(3) 24240·1	(9) 24358·3	
⁴P₂ 417·2	(7) 24342·9	(6) 23360·9	(8) 24629·3
⁴P₃		(8) 24877·7	(10) 25046·1
⁴S₂	(1) 26156·8	(1) 26275·2	—

³ Bloch, Ann. de Phy. 8, 897 (1927).

It is interesting to note here that the P-terms belonging to $2M_2M_3$ are inverted, while all other terms so far found by Bowen and by the present authors (see Table II) are direct.

TABLE II.

$$2M_2(N_2 \longleftarrow N_3)$$

$2M_2N_3$ $2M_2N_2$	$^4F_2$	$^4F_3$ 224·1	$^4F_4$ 344·0	$^4E_5$ 492·4	$^4D_1$
$^4D_1$	(4) 38432·2				(3) 40456·8
258·6					
$^4D_2$	(2) 38174·2	(4) 38398·2			(8) 40199·4
433·1					
$^4D_3$	(0) 37740·8	(3) 37964·1	(5) 38308·9		
602·5					
$^4D_4$		(0) 37367·3	(8) 37707·3	(4) 38199·7	
$^4P_1$	—				(4) 37504·6
102·4					
$^4P_2$	—	(1) 35606·5			
417·2					
$^4P_3$	(1) 34957·9	(2) 35183·0	(1) 35533·9		

It will be seen that the term $^4F_5$ can combine only with $^4D_4$, giving only one line. This term, has, therefore, been obtained by comparing the above F-differences with those in the spectrum of S II. The spectrum of S II has recently been classified by Bhattacharyya[4] and by Ingram.[5] In Table III are given the F-differences in the spectra of S II and Cl III and

[4] Bhattacharyya, Nature, 122, 241 (1928).

[5] Ingram, Phy. Rev., 32, 172 (1928).

their corresponding ratios. It is found that if we choose the line $\nu = 38199\cdot7$ as $^4D_4 - {}^4F_5$, the ratios are approximately the same.

TABLE III.

Difference.	S II.	Cl III.	Ratio.
$^4F_2 - {}^4F_3$	184·9	224·1	1·66
$^4F_3 - {}^4F_4$	210·3	344·9	1·64
$^4F_4 - {}^4F_5$	310·6	492·4	1·59

TABLE IV.

Term values.

$2M_2M_3$ $^4P_1$		142154·5
$^4P_2$		142272·6
$^4P_3$		142440·7
$2M_3N_3$ $^4F_3$		82430·1
$^4F_4$		82206·0
$^4F_5$		81861·1
$^4F_6$		81868·7
$^4D_1$		80406·7

The following is the list of lines classified.

TABLE V.

λ	In	ν (vac.)	Classification.
			$2M_2M_2-2M_2N_2$
2471·03	3	40456·7	$^4D_1-^4D_1$
2486·85	3	40199·4	$^4D_2-^4D_1$
2601·21	4	38432·2	$^4D_1-^4F_2$
2603·51	4	38398·2	$^4D_2-^4F_3$
2609·58	5	38308·9	$^4D_3-^4F_4$
2617·04	4	38199·7	$^4D_4-^4F_5$
2618·79	2	38174·2	$^4D_4-^4F_3$
2633·28	3	37964·1	$^4D_3-^4F_3$
2648·86	0	37740·8	$^4D_2-^4F_2$
2651·22	3	37707·3	$^4D_4-^4F_4$
2665·55	4	37504·6	$^2_2P_1-\ D_1$
2675·34	0	37307·3	$^4D_4-^4F_3$
2807·65	1	35606·5	$^4P_3-^4F_3$
2813·39	1	35533·9	$^4P_3-^4F_4$
2841·45	2	35183·0	$^4P_3-^2F_3$
2859·75	1	34957·9	$^4P_4-^4F_3$
			$2M_2N_2-2M_2N_2$
3804·80	1	26275·2	$^4P_{\overline{3}}-^4S_{\overline{3}}$
3822·01	1	26156·8	$^4P_1-^4S_{\overline{3}}$
3991·52	10	25046·1	$^2_2P_3-^4P_3$
4018·53	8	24877·7	$_{11}P_{\overline{3}}-^4P_3$
4059·07	8	24629·3	$^4P_4-^4P_3$
4087·01	6	24460·9	$^4P_3-^4P_3$
4104·22	9	24358·3	$^4P_{\overline{3}}-^4P_1$
4106·82	7	24342·9	$^4P_1-^4P_{\overline{3}}$

TABLE V—contd.

λ	Int.	ν (vac.)	Classification.
4124·24	3	24240·1	$^4P_1 - ^4P_1$
4370·92	8	22872·1	$^4P_3 - ^4D_4$
4489·21	2	22269·4	$^4P_3 - ^4D_3$
4523·38	5	22101·2	$^4P_2 - ^4D_2$
4613·67	3	21666·7	$^4P_2 - ^4D_2$
4695·33	1	21291·8	$^4P_1 - ^4D_1$

We are very thankful to Prof. M. N. Saha, D.Sc., F.R.S., for his interest in this work.

PHYSICS DEPARTMENT,
UNIVERSITY OF ALLAHABAD,
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The Spectrum of Carbon

BY

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The spectra of C, C+, C++ and C+++ have attracted the attention of several investigators during recent years, both from theoretical and experimental points of view. As a result of experimental investigation of the spectra large amount of data have been collected by different workers (Millikan,[1] Bowen, Simeon,[2] Hutchinson,[3] Merton and Johnson,[4] Ryde,[5] Lamg,[6] Fowler[7] and others) and classified on the series basis. A survey of the different lists shows that the values of the wave-lengths given by the different observers do not always agree ; moreover a very large number of lines remain unaccounted for.

A very brief survey of the work hitherto done may be given here.

Spectrum of C+++.—Only four lines have been attributed to C+++ and classified by Millikan.

Spectrum of C++.—The identification of C++ lines and their classification is given by Millikan and Bowen. Very recently Fowler has attributed a few more lines to C++: The total number of C++ lines hitherto known is about 20.

[1] Millikan and Bowen, Astrophys. J., 53, p. 150.
[2] Simeon, Proc. Roy. Soc. A., 102, p. 484.
[3] Hutchinson, Astrophys. J., 58, p. 280.
[4] Merton and Johnson, Proc. Roy. Soc. A., 103, p. 884 ; Johnson, Proc. Roy. Soc. A., 108, p. 848.
[5] Ryde, Proc. Roy. Soc., 117, p. 164.
[6] Lamg, Roy. Soc. Phil. Trans., 224, p. 371.
[7] Fowler, Proc. Roy. Soc., 118, p. 82 ; 120, p. 812.

Spectrum of C^+ .—An analysis of C^+ spectrum was given by Fowler some years ago, and later by Bowen. In a very recent paper Fowler has very critically re-investigated the spectrum of C^+ and has accounted for a large number of lines as forming doublet combinations and quartet combinations.

Spectrum of C .—The fundamental triplets in the spectrum of C (CI) were identified by Bowen and McLennan some time ago. Last year Fowler and Selwyn after an experimental investigation of the CI spectrum obtained many new lines. They analysed a large number of CI lines.

In Bowen's and Fowler's analyses of Carbon only the fundamental lines of the triplet system and the singlet system have been obtained, but no intercombinations between the two systems have yet been traced.

In view of Bowen's interesting discovery that the lines ascribed to Nebulium really belong to O^{++}, N^+,—and correspond to forbidden transitions amongst the fundamental Singlet and Triplet levels, and Saha's hypothesis that the lines attributed to Coronium may be due to similar forbidden transitions in the spectra of C, N, or P^+, S^+, etc., I undertook an investigation to trace intercombinations between levels of different multiplicity in spectra of light elements. Taking the spectra of elements having 2 p-valence electrons, *viz.*, C, Si, Ge, Sn, and Pb, we find that intercombinations become stronger (as first pointed out by Krönig) with higher atomic weights. From Pb we can easily trace them up to Silicon. In Carbon, intercombinations have not yet been traced.

With the view therefore to seek for intercombinations in the spectrum of Carbon, I undertook an investigation of the spectrum. The method used was to take the spectrum of the heavy-current Carbon arc. (Dr. N. K. Sur showed that the forbidden lines of Pb can easily be obtained in the laboratory in this way.) With Silver spark for comparison several photographs were taken, on everyone of which the new lines

recorded in the Table I below were obtained though fainter on some than on others. Schumann plates were used for taking photographs of the spectrum. The wave-lengths are given in Rowland system, the frequencies of course are ν vac.

TABLE I.

Wave-lengths (Rowland system).	ν vac.	Remarks.
1930,4	51785,9	Fowler 1931,027 λ vac.
1933,5	51703,6	McLennan 1933
1935,7	51644,9	
1938,3	51575,6	
1946,6	51355,8	$^1\overline{D}_2 - {}^3\overline{P}_2$ ⎤
1948,2	51313,6	$^1\overline{D}_2 - {}^3\overline{P}_1$ ⎦ $2L_2 \longleftarrow L_2 M_1$
1955,3	51127,4	McLennan λ 1955, Hutchinson λ 1954,1
1973,0	50668,8	$^3\overline{P}_0 - {}^3\overline{P}_1$
1973,9	50645,7	$^3\overline{P}_1 - {}^3P_1$
1974,8	50622,7	
1975,6	50602,2	$_3\overline{P}_2 - {}^3P_1$
1976,8	50571,5	
1977,8	50545,9	$^3\overline{P}_1 - {}^3P_2$
1978,7	50522,9	
1979,6	50499,9	$^3\overline{P}_2 - {}^3P_2$
1980,8	50469,4	
1981,8	50443,9	
1982,9	50415,9	
1984,2	50382,9	
1985,3	50355,0	
1986,8	50329,7	
1987,5	50299,3	
1988,7	50271,5	
1990,9	50218,4	
1993,3	50154,2	$^1\overline{P}_4 - {}^5P_1$
2002,0	49985,9	

Wave-lengths (Rowland system).	v vac.	Remarks·
2002,6	49920,1	$^3\overline{P}_0 - {}^3\widetilde{D}_1$
2003,9	49887,7	
2005,2	49855,4	$^3\overline{P}_2 - \overline{D}_1$
2006,4	49825,6	
2007,7	49793,4	$^3\overline{P}_1 - {}^3\overline{D}_2$
2009,3	49753,7	$^3\overline{P}_2 - {}^3\overline{D}_3$
2010,4	49726,5	
2011,6	49696,8	
2012,8	49667,2	
2014,0	49637,6	
2015,3	49605,6	
2016,8	49581,0	$^3P_2 - {}^3\overline{D}_3$
2020,0	49490,2	O^+ ? $\left[\begin{array}{l}\text{McLennan } \lambda\ 2020. \\ \text{Hutchinson } \lambda\ 2020\cdot2\end{array}\right]$
2021,7	49451,1	O^+ ?
2023,0	49416,9	$^1\overline{P}_1 - {}^3\overline{D}_1$
2024,4	49382,7	
2027,4	49309,7	$^1\overline{P}_1 - {}^3\overline{D}_2$
2028,5	49282,9	
2029,2	49265,9	
2047,8	48830,5	
2120,0	47156,4	Si ?
2148,8	46524,6	O^+ ?
2190,5	45639,1	O^+ ?
2208,4	45269,3	
2211,6	45203,8	
2217,4	45097,8	
2312,9	43224,5	
2322,5	43045,0	O^+ ? Fe$^+$?

Wave-lengths (Rowland system).	ν vac.	REMARKS.
2354,6	42458,3	2354,12 Rydes, 2353,22
2435,5	41048,1	O+ ? Si ?
2479,8	40315,1	{Reversed and broadened very much. 2478,525 M. and J.
2498,3	40016,7	N+ ?
2507,7	39866,7	
2514,0	39766,8	
2523,3	39620,3	N+ ?
2528,9	39532,6	Si ? O+ ?
2582,3	38715,2	Fe+ ? [Fowler 2582·85. Johnson 2582·9
2590,0	38586,7	N+ ?
2598,3	38476,8	Fe+ ?
2629,6	38018,9	
2676,0	37459,8	
2688,4	37187,5	
2699,9	37029,1	
2703,9	36974,3	
2794,7	35773,0	
2800,8	35695,1	
2837,3	35296,0	C+ 2837,71 Fowler, 2837,60
2851	35066,6	
2881,5	34695,5	O ? Fe ?
2892,6	34562,3	O ? Fe ?
2909,4	34362,7	
2924,7	34183,0	Fe ?
2930,6	34114,2	

Discussion of Results.

The analysis of CI. Spectrum is partly due to Bowen and partly to Fowler. The triplet combinations $(L_2 \leftarrow M_1)$ $^3P—^3P$ and $(L_2 \leftarrow M_3)$ $^3P—^3D$ and also the inner-transition triplet combinations $(2L_2 \leftarrow L_1 3L_2)$ $^3P—^3\overline{P}$ and $^3P—^3D$ are due to Bowen. They have been confirmed by Fowler. The rest of the analysis and assignment of term values is mainly due to Fowler. The classifications, of some of the old lines and some of the new lines, forming a part of this paper are given within brackets, [   ] in Table II below in which only the analysis of the $2L_2 \leftarrow L_2 M_1$ and $2L_2 \leftarrow L_1 3L_2$ is given out of the analysis of Fowler and Bowen.

TABLE II.

Spectrum of Carbon.

$L_2 L_2$	$L_2 M_1$	30019 $^3\overline{P}_0$ 20	29999 $^3\overline{P}_1$ 41	29959 $^3\overline{P}_2$ 4 32	29526 $^1\overline{P}_1$
90350	$^3P_0$		60349·7		
	15				
90335	$^3P_1$	60316·5	60336·6	60376·6	
	27·5				
90308	$^3P_2$		60308·9	60349	
	8996			—	
81312	$^1\overline{D}_2$		*(1948·2) [51313·6]	*(1946·6) [51355·8]	(1931·027) 51785·9
	11451				
69860	$^1\overline{S}_0$	•	*(2507·7) [39862]		(2478·53) 40334·4

* These wave-lengths are given in Rowland system.

TABLE II (contd.).

$L_{1,3}L_2$ / L_1L_2	³S	26258 ³D₁	26260 ³D₂	26262 ³D₃	³P̄₀	15097 ³P₁	³P₂	14730 ¹P̄₁	11774 ³S₁	11508 ¹D₂
90350 ³P₀		(1560·267) 64091				75253				
15										
90335 ³P₁			(1560·66) 64075·5			75238		(1322·6) [75605]	(1272·9) [78561]	(1768·6) [78827]
27										
90308 ³P₂				(1561·3) 64045·9		75211·7				
81312 ¹D̄₂								(1501·9) [66582]		(1432·6) [69804]
69860 ¹S̄₀						(1826) [54767·7]		(1813·8) [55132]	(1721·5) [58087]	

On trying to classify some of the new lines obtained in my experiment it was found that the lines λ 1946,6, 1948,2 and 2507,7 do very correctly represent the inter-combination lines $^1\overline{D}_2 - {}^3\overline{P}_{1,\,2}$ and $^1\overline{S}_0 - {}^3\overline{P}_1$ respectively giving the difference of 11451 between λ 1948·2 and λ 2507·7, which is the difference between the two fundamental singlet lines λ 1931·027 and λ 2478·53. (Fowler has classified a line 2509,11 as the $(L_1 2L_2 \leftarrow 3L_2)$ inner-transition line $^2P_1 - {}^2D_2$ of C.$^+$). Taking our identifications as correct and taking Fowler's value of $(2L_2)^1\overline{D}_2$ as more reliable, the values of the terms $(2L_2)3P$ and $(L_2M_1)3\overline{P}_1$ so also of the terms of $L_1 3L_2$ are required to be reduced by about 667 units. These values are given in the tables. The difference between the $^3P_1$ and $^1\overline{S}_0$ of $2L_2$ is 20474. With these modified values of the terms an identification of inner-transition lines $(2L_2 \leftarrow L_1 3L_2)$ was attempted, and the combination lines of $(L_1 3L_2)$ $^1D_2$, $^1\overline{P}_1$, $^3S_1$ with the $2L_2$ terms were obtained (as shown in the table) with considerable inambiguity. The line λ 1827 can be reasonably classified as inter-combination line of the inner-transition $(2L_2 \leftarrow L_1 3L_2)$ $^1\overline{S}_0 - {}^3\overline{P}_1$. The term values of $(L_1 3L_2)$ $^1D_2$, $^3S_1$, $^1P_1$ would be

$^1P_1$	14730.
$^3S_1$	11774.
$^1D_2$	11508.

In the recent paper on the spectrum of C$^+$ Fowler has identified the inner-transition $(L_1 2L_2 \rightarrow 2L_1 L_2)$ the approximate average difference between the terms corresponding to these states being about 51000. On a suggestion from Dr. Saha I attempted to search for inner-transitions in the spectrum of CI of the type $(2L_1 L_2 M_1 \leftarrow L_1 2L_2 M_1)$ which roughly correspond to the inner-transitions in C$^+$ giving the difference of about 51000 in the term values. The following table gives the results of the attempt of analysis on the above line of argument.

TABLE III.

The values of the $^3\bar{D}_1$ and $^8P_1$ terms of $L_1 2L_2 M_1$ are obtained as negatives. They will be

$^3P_0$ [−20695].	$^3\bar{D}_1$ [−19897]
$^3P_1$ [−20645]	$^8\bar{D}_2$ [−19793]
$^3P_2$ [−20545].	$^3D_2$ [−19623]

approximately. The discrepancy in not obtaining exact frequency differences is due to the degree of inaccuracy in the wave-length determinations in my experiment.

The $(2L_1 L_2 M_1 \longleftarrow L_1 2L_2 M_1)$ inner-transition lines of Carbon.

$2L_1 L_2 M_1$	30019 $^3\bar{P}_0$ 20	29999 $^3\bar{P}_1$	29958 $^3\bar{\bar{P}}_2$ 41	29526 $^3\bar{P}_1^-$ 432
$L_1 2L_2 M_1$	......	......	......	......
$^3\bar{P_0}$ (−20695)	......	......	......	......
$^3P_1$ (−20645)	50668	50645	50602	50154
$^3P_2$ (−20545)	......	50545	50500	......
$^3\bar{D}_1$ (−19897)	49920	......	49855	49417
$^3\bar{D}_2$ (−19793)	......	49793	49753	49310
$^3\bar{D}_2$ (−19623)	......	......	49581	......

List of Classified Lines.

A total list of lines classified by me is given below. It includes classification of some of the old lines and of some of the new lines obtained in my experimental investigation.

2

Lines obtained in this Experiment.

Wave-length.	Wave-number.	Classification.
1946,6	51355,8	$^1\bar{D} - ^3\bar{P}_2$
1948,2	51313,0	$^1\bar{D}_2 - ^5\bar{P}_1$ $\}(L_2M_1 \longleftrightarrow L_2L_3)$
1973,0	50668,8	$^5\bar{P}_0 - ^3P_1$
1973,9	50645,0	$^3\bar{P}_1 - ^3P_1$
1975,6	50602,2	$^3\bar{P}_2 - ^3P_1$
1977,8	50545,9	$^3\bar{P}_I - ^3P_2$ $(L_12L_2M_1 \longrightarrow 2L_1L_2M_1)$
1979,6	50500,0	$^3\ddot{P}_2 - ^3P_2$
1993,3	50154,2	$^1\bar{P}_1 - ^3P_1$
2002,6	49920,1	$^3\bar{P}_0 - ^3\bar{D}_1$
2005,2	49855,4	$^3\dot{P}_2 - ^3\bar{D}_1$
2007,7	49793,4	$^3\dot{P}_1 - ^3\bar{D}_2$
2009,3	49753,7	$^3\bar{P}_2 - ^3\bar{D}_2$ $\}(L_12L_2M_1 \longrightarrow 2L_1L_2M_1)$
2016,3	49581,0	$^3\bar{P}_2 - ^3\bar{D}_3$
2023,0	49416,9	$^1\bar{P}_1 - ^3\bar{D}_1$
2027,4	49309,7	$^1\bar{P}_1 - ^3\bar{D}_2$
2507,7	39862	$^1\bar{S}_0 - ^3P_1$ $\bar{L}_2M_1 \longrightarrow L_2L_3$
1268,6*	78827	$^3P_1 - ^1D_1$
1272,9*	*78561	$^3P_1 - ^3S_1$ $\}L_1{}^3L_2 \longrightarrow 2L_12L_1$
1296,7*	77120	$^3P_1 - X$

Lines already obtained.

Wave-length.	Wave-number.	Classification.
1322,6*	75605	$^3\bar{P}_1 - {}^1P_1$ ⎫
1432,6*	69804	$^1\bar{D}_2 - {}^1D_2$ ⎬ $L_1 3L_2 \longrightarrow 2L_1 2L_2^3$
1468,5*	68097	$^1\bar{D}_2 - X$
1501,9*	66582	$^1\bar{D}_2 - {}^1P_1$ ⎫
1721,5*	58087	$^1\bar{S}_0 - {}^3S_1$ ⎬ $L_1 3L_2 \longrightarrow 2L_1 2L_2$
1765,1*	56644	$^1\bar{S}_0 - X$
1813,8*	55132	$^1\bar{S}_0 - {}^1\bar{P}_1$ ⎫
1826 ?*	54768	$^1\bar{S}_0 - {}^3\bar{P}_1$ ⎬ $L_1 3L_2 \longrightarrow 2L_1 2L_2$

A more critical investigation is intended to be undertaken, and it is hoped some more results and useful clues may be obtainable from it. In the photographs that I obtained I could not do measurements of some lines on account of their being so faint that they could not be observed with any definiteness under the comparator. The wave-lengths also need to be determined with a greater degree of accuracy. One point has escaped mention that I have obtained no lines (as will be evident from the list) of C^{+3}, C^{++}, or C^+, except the pair of lines at λ 2837 (unresolved in my plate).

Lines already obtained.

An Attempt to detect a Undirectional Effect of X-Rays

By
Arthur H. Compton, K. N. Mathur and H.R. Sarna.

It has been shown by Bubb[2] that a polarized beam of x-rays ejects photoelectrons whose most probable direction of emission lies in the plane of the electric vector of the polarized waves. If we picture the x-rays as consisting of a stream of photons, each of which is capable of ejecting a photoelectron, this may be explained by assigning to each photon certain vector characteristics and a definite orientation. Such was Bubb's interpretation of his experimental results.

In the case of polarized radiation, however, the electric vector though in a definite direction alternates between a positive and negative sense in this direction. Expressing this in terms of vector photons, a plane polarised electromagnetic wave would be represented by successive groups of photons oriented alternately parallel and antiparallel to a fixed line in the plane of the electric vector. The question arises, is it possible to obtain radiation with an excess of photons oriented in one sense in the plane of polarization? If such a unidirectional property could be detected, it would be a qualitatively new phenomenon in optics.

It would seem that the rays coming directly from the target of an x-ray tube might have such unidirectional characteristics. According to Stokes' theory, these x-rays are produced by the sudden stopping of the cathode electrons when

An abstract of this paper has appeared in the Physical Review, 31, 159 (January, 1928).

F. W. Bubb, Phys. Rev., 23 137 (1924).

they reach the target, in which case the electric vector and the corresponding photons should be strictly unidirectional. On Kramers' view,[8] the impinging electron radiates while coursing in a hyperbolic orbit about the nucleus of an atom in the target. In this case also there should be a larger component of the electric vector of the resulting ray anti-parallel to the cathode ray stream than parallel to it.

When examined more closely, however, it is by no means certain that theory demands such a unidirectional property of the x-rays. In the case of the part of the rays which gives rise to the line spectrum, it is evident that in order that sharp lines may appear it is necessary that there shall be long trains of waves, that is, alternate groups of photons oriented in opposite directions. But the continuous spectrum also has its sharp upper limit of frequency, which means a complete interference at small glancing angles from the crystal such as can occur only with long trains of waves. Furthermore the studies of electromagnetic pulses by J. J. Thomson and Sommerfeld have shown that when unidirectional pulses traverse a thin layer of matter their asymmetry is rapidly reduced. From the photon standpoint, however, it is not obvious that a sharp frequency limit will mean anything more than photons with a fixed maximum of energy, and the attempt to detect such a unidirectional property of the x-rays does not appear hopeless.
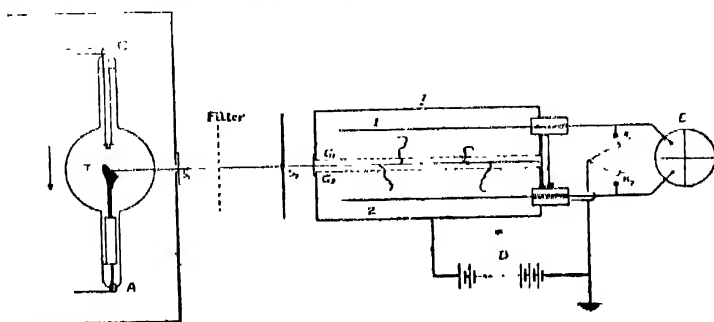
Fig. 1.

[8] H. A. Kramers, Phil, Mag., 46, 836 (1923).

The experiment was performed as shown diagrammatically in Figure 1. X-rays from a "universal type" Coolidge tube, placed in a horizontal position, passed through two narrow vertical slits S_1, S_2, and into an ionization chamber I. The x-rays formed a thin sheet between two gauzes G_1 and G_2. If the x-rays resulting from the stopping of a cathode ray form a pulse, as Strokes suggests, the direction of the electric vector of this pulse at the ionization chamber should be such as to exert a force on an electron in the direction $G_1 \longrightarrow G_2$. We might thus anticipate a greater number of photo-electrons in the side 2 of the chamber than in the side 1. As will be seen from the figure, the electrodes 1 and 2 are connected to opposite pairs of quadrants of a Dolezalek electrometer. Thus if more photo-electrons enter one side of the chamber than the other, producing greater ionization, there will be a corresponding deflection of the electrometer.

It was found that the readings were rather sensitive to changes in the location of the x-ray beam between the two gauzes. This required an accurate alignment of the slits and of the chamber itself. Some difficulty was also experienced due to the uneven brilliance of different portions of the focal spot. This resulted in an unsymmetrical sheet of x-rays between the gauzes, the dissymmetry varying with the position of the target of the tube. Errors due to this source were reduced by making the slits narrow. In order to eliminate systematic errors, alternate readings were taken with the tube reversed in direction.

Experiments were tried at tube potentials from about 40 to about 100 kilovolts, with and without filters placed in the path of the x-rays. In some preliminary experiments it appeared that an effect of about 5 per cent. in the predicted direction was present, and this provisional result was described at the meeting of the All-India Science Congress held in Lahore in January, 1927. Later, more refined experiments failed to show any consistent change in the ionization in the

two halves of the chamber when the x-ray tube was reversed. It appeared that the positive result of the earlier experiment was due to the dissymmetry of the x-ray beam described in the paragraph above. When the slits were made narrower no such effect was observed.

The results of our final experiments may be summarized by the statement that on reversing the x-ray tube, no dissymmetry in the ionization current appeared which was larger than the probable error of our measurements, about 1 part in 500.

It would be premature to conclude from this negative result that the photon does not possess the vector properties of a line in a definite direction. The possibility is clearly present that the conditions of our experiment were not suitable to ensure any predominance of the photons oriented in one sense. If, however, it is essentially impossible to produce radiation in which the electric vector or the protons directed in one sense can be distinguished from those in the opposite sense, the sense of the electric vector as well as of the photon ceases to have any significance. In this regard the electric field of radiation would be different in quality from a static electric field.

On the Electric Moment of Primary Alcohols

By

P. C. Mahanti, M.Sc., and R. N. Dasgupta, M.Sc.

Abstract.

The paper deals with the determination of electric moments of a number of primary alcohols by the well-known bridge method. The value obtained for each alcohol is nearly the same, thus indicating that the oxygen atom of the OH group in alcohols is similarly polarised.

Introduction.

The idea of the molecular polarisation introduced by Debye[1] has rendered it possible to calculate the permanent electric moments of the molecules of a substance from the dielectric constant and density data provided they are dissolved in a solvent which has no electric moment. It has been pointed out by L. Lange,[2] Williams and Krchma [3] and very recently by J. Rolinski[4] that liquids such as carbon tetrachloride, carbon bisulphide, pentane, hexane and benzene should act as suitable solvents of this type and it has also been verified by them that mixtures of various dipole liquids in these solvents strictly obey Debye's Law. The purpose of this paper is to present the results of calculation of the electric moments of a large number of primary alcohols

[1] Debye, Phys. Zeits., 13, 97, 1912 ; Handbuch der Radiologie, 6, 625, 1925.
[2] Luise Lange, Zeits., f Physik, 33, 169, 1925.
[3] Williams and Krchma, Am. Chem. Soc. Jour., 49, 1676. 1927.
[4] Rolinski, Phys. Zeits., 29 658, 1928.

from measurements of the dielectric constants and densities of their solution in benzene.

It is a well-known fact that, if a binary mixture consists of a dipole-free liquid (B) obeying Clausius-Mosotti law and a dipolar liquid (A) obeying Debye's law, then at a definite temperature the general additive law of polarisation should be satisfied for different concentrations if the molecules of the two liquids do not react upon one another. Any deviation from the additive law has been attributed to the association of the liquid molecules among themselves. Thus the molecular polarisation of such a given mixture is expressed by

$$P_{AB} = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M_A C_A + M_B C_B}{d_{AB}} \qquad \ldots \qquad \ldots \qquad (1a)$$

$$= P_A C_A + P_B C_B \qquad \ldots \qquad \ldots \qquad \ldots \qquad (1b)$$

where ϵ = dielectric constant of the mixture having density d_{AB} at the room temperature.

M_A, M_B = molecular weights of the solute (alcohol) and solvent (Benzene)   respectively.

C_A, C_B = molecular fractions of   ,,   ,,

P_A, P_B = molecular polarisation   ,,

But according to Debye,

$$P_A = \frac{4\pi}{3} N \left(\gamma_A + \frac{\mu^2}{3\kappa\tau} \right) \qquad \ldots \qquad \ldots \qquad (2)$$

where N = Avogadro number,

γ_A = molecular polarisability,

μ = electric moment,

κ = Boltzman constant,

τ = absolute temperature,

According to Lorenz-Lorentz law,

$$\frac{4\pi N}{3} \gamma_A = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M_A}{d_A}$$

$$- \frac{n_A{}^2-1}{n_A{}^2+2} \cdot \frac{M_A}{d_A} \qquad \ldots \qquad (3)$$

Where n_A, d_A = refractive index and density respectively of the alcohol at room temperature.

Also from (1b)

$$P_A = \frac{P_{AB} - P_D \; C_B}{C} \qquad \dots \quad (4)$$

Hence combining equations (2), (3) and (4) the electric moment μ of the solute molecule, can be calculated.

Experimental :—

For the determination of dielectric constants of liquids which are even feebly conducting it is clear that any method using resonance would lead to erroneous values unless some arrangement is provided by which the current flow due to conduction is somehow neutralised. Hence, some method in which a sharp null point could be detected is preferable to the usual coupled circuit beat method used for gases and vapours which are perfect insulators.

The Nernst bridge arrangement is therefore used in this investigation. The necessary condition of silence in the telephone which is used as detector is secured when the leads from the telephone are connected to points which should not only be at the same potential but also where the condition of the phases of the two alternating e. m. f's. should be the same. Since the phase angle depends on the resistance, inductance and capacitance in the arms; a balance of resistance and inductance is therefore required along with a balance of capacitance. This is obtained by the simultaneous adjustment of capacitance and resistance in the proper arm of the bridge. Hence determination of the capacitance is made as if the resistances were not there.

The source of alternating current is a microphone hummer at 1000 frequency. In the case of capacitance of appreciable dielectric loss the point of minimum audibility is somewhat indefinite. This is made more critical by using a

variable resistance in series with the capacitance. This variable resistance is a liquid resistance of Magnanini solution. Pure mannito-boric acid crystals were prepared by dissolving 12 gms. of mannitol and 8·2 gms. of boric acid in 95 c.c of absolute alcohol and setting the solution aside for a few days in a cold place—the first few crystals formed were discarded and those subsequently deposited were taken. These crystals were finally dissolved in distilled water to get the Magnanini solution. The apparatus was well earthed.

The experimental condenser is of parallel plate type and the outer plate system is well insulated from the inner plate system by mica rings. It was first carefully calibrated by using benzene, ethyl ether and octane. The capacity was thus found to be 36·32 $\mu\mu$F.

The chemicals used in the investigation were brought from Kahlbaum (purest) and were carefully distilled and dried before use. Special care was taken to have the measurements only with dilute solutions of the alcohols in benzene as it has been already pointed out by Debye that at higher concentrations there is chance of association between the solute and the solvent molecules. The density of each solution was determined by means of a delicate chemical balance and pyknometer. The refractive indices of the alcohols were measured with the help of Abbe Refractometer. Special care was taken to avoid vaporisation during weighing, etc.

The experimental condenser is connected in parallel to the arm of the bridge containing the standard variable condenser. The change of capacity of the experimental condenser due to the introduction of the solution is determined from the readings on the standard condenser. Thus the dielectric constant of the solution is calculated from the relation

$$\epsilon - 1 = \frac{\triangle C}{C_o} \qquad \ldots \qquad \ldots \qquad \ldots \quad (5)$$

$$= \frac{\triangle c}{36 \cdot 32}.$$

After each measurement the experimental condenser and the vessel containing it were carefully washed and dried.

The precision standard condenser used in the investigation is the Bureau of Standards pattern variable air condenser manufactured by Leeds and Northrup. A certificate of standardisation indicates the values of the capacity corresponding to divisions marked on the dial. A slow adjustment screw permits the reading of the capacity within $0 \cdot 05$ $\mu\mu$F and the values are accurate to within $\pm$ $1\mu\mu$F. The maximum capacity of the condenser is 1134 $\mu\mu$F.

Experimental results :—

For each solution, C_A and C_B in the equation (1a) were calculated from the following relation. Thus

if m_A gms. of alcohol is dissolved in m_B gms of benzene, then

$$Z_A = \frac{m_A}{M_A} \text{ and } Z_B = \frac{m_B}{M_B} \qquad \ldots \qquad \ldots \qquad \ldots \quad (6)$$

$$\therefore \quad C_A = \frac{Z_A}{Z_A + Z_B} \text{ and } C_B = \frac{Z_B}{Z_A + Z_B} \qquad \ldots \qquad \ldots \quad (7)$$

Knowing the value of ϵ for the solution, P_{AB} was calculated from the equation (1a).

All measurements were made at the room temp. (25°C).

TABLE I.

Solute	C_A	d	ϵ	P_{AB}
	0	0·872	2·26	26·46
	3·01	0·871	2·38	28·16
n-Butyl Alcohol, C_4H_9OH	7·69	0·867	2·47	29·47
	11·56	0·863	2·59	30·63
	15·95	0·859	2·80	33·78
	19·56	0·857	2·95	35·49
	24·98	0·858	4·54	41·40

TABLE I. (Continued).

Solute	C_A	d	ϵ	P_{AB}
n-Hexyl Alcohol, $C_6H_{13}OH$	0	0·872	2·26	26·46
	2·75	0·870	2·35	28·05
	5·21	0·866	2·44	29·68
	7·76	0·864	2·50	30·81
	12·56	0·862	2·59	32·56
	17·49	0·854	2·80	36·10
	24·55	0·850	3·22	41·97
n-Octyl Alcohol, $C_8H_{17}OH$	0	0·872	2·26	26·46
	2·42	0·870	2·36	28·59
	3·50	0·867	2·40	29·00
	4·98	0·865	2·45	30·25
	7·26	0·861	2·52	31·98
	9·51	0·856	2·61	33·81
	11·30	0·851	2·67	35·20
	15·26	0·844	2·82	38·45
n-Nonyl Alcohol, $C_9H_{19}OH$	0	0·872	2·26	26·46
	4·12	0·870	2·36	28·87
	7·12	0·862	2·47	31·56
	10·67	0·859	2·55	33·73
	15·52	0·853	2·69	37·29
	19·15	0·849	2·74	39·23
n-Decyl Alcohol, $C_{10}H_{21}OH$	0	0·872	2·26	26·46
	3·49	0·866	2·32	28·47
	7·69	0·863	2·44	31·63
	12·49	0·857	2·62	35·99
	16·94	0·851	2·74	39·49
	20·28	0·849	2·80	41·64

Calculation of the Electric Moments of the Molecules.

For each solute a graph was drawn showing the relation between C_A and P_{AB}. Then from the graph, $P_A C_A$ was obtained from the relation $P_A C_A = P_{AB} - P_B C_B$ the values of P_B when $C_B = 100$ and when $C_B = 0$ being known for benzene and a straight line being drawn on the same graph joining these two points. The ordinate corresponding to any point on this straight line gives the values of $P_B C_B$ for benzene. Then P_A for each concentration of the solute was found by dividing $P_A C_A$ by C_A. Finally a graph was drawn showing the relation between C_A and P_A. The value of P_A when C is infinitesimal is the ordinate corresponding to $C_B = 100$.

As it has been indicated in equation (2) the molecular polarisation of each solute contains two terms, a polarisation due to an orientation effect, P_A' and a polarisation due to the deformation effect, P_A''. Since the polarisation due to the deformation of the molecule may be approximated by the familiar Lorenz-Lorentz formula, the polarization due to the orientation effect may be calculated. This term contains the electric moment of the solute molecule, μ as follows :—

$$P_A' = \frac{4\pi \ Nv^2}{3 \cdot 3KT}$$

$$= 20 \ 71 \times 10^{36} \ \mu^2 \qquad \qquad \dots \quad (8)$$

$$[N = 6 \cdot 06 \times 10^{23}; \ K = 1 \cdot 37 \times 10^{-16}; \ T = 298.]$$

Thus for the n-Butyl alcohol,

$$P_A = 76 \cdot 5 \pm 4 \ \text{c.c. from the graph}$$

and $$P_A'' = \frac{n_A^2 - 1}{n_A^2 + 2} \cdot \frac{M_A}{d_A} = 22 \cdot 11 \ \text{c.c.}$$

$$\therefore P_A' = P_A - P_A'' = 76 \cdot 5 - 22 \cdot 11 = 54 \cdot 39 \ \text{c.c.}$$

Hence $54 \cdot 39 = 20 \cdot 71 \times 10^{36} . \ \mu^2$,

$$\therefore \mu = (1 \cdot 62 \pm \cdot 06) = 10^{-18},$$

TABLE II.

Chemical formula.	d	n	P_A	P_A''	P_A'	$\mu \times 10^{18}$
C_4H_9OH ...	0·810	1·399	76·5 c.c.	22·11 c.c.	54·39 c.c.	1·62
$C_5H_{12}OH$ ...	0·833	1·418	86·0 ,,	30·61 ,,	55·39 ,,	1·64
$C_8H_{17}OH$ ...	0·839	1·424	95·5 ,,	39·59 ,,	55·91 ,,	1·64
$C_9H_{19}OH$ ...	0·842	1·442	98·3 ,,	45·27 ,,	53·03 ,,	1·60
$C_{10}H_{21}OH$ ..	0·844	1·446	104·0 ,,	49·90 ,,	54·10 ,.	1·61
$C_{11}H_{23}OH$ ...	0·833	1·441	112·0 ,,	54·55 ,,	57·45 ,,	1·66
$C_{12}H_{25}OH$ ...	0·830	1·440	113·0 ,,	58·91 ,,	54·09 ,,	1·62
$C_6H_5CH_2CH_2OH$ ...	0·995	1·526	93·0 .,	37·61 ,,	55·39 ,,	1·64
$C_6H_5CH_2CH_2CH_2OH$ ...	0·990	1·525	97·0 ,,	42·10 ,,	54·90 ,,	1·63

Discussion.

The results clearly indicate that so far as the primary alcohols are concerned they have practically the same dipole-moment in them. Since these alcohols are produced by the substitution of one atom of hydrogen by an OH group in normal hydro-carbon molecules, it is reasonable to infer that the electric moment is due to the polarisation of the oxygen atom by the hydrogen atom on the one hand and by the carbon atom on the other. In other words it may be stated that the binding forces acting on the carbon atom reacting with the oxygen atom is just the same whether the chain is long or short, open or closed.

The values for the electric moments of other primary alcohols obtained by different observers at different times point to the same fact. Thus

Methyl Alcohol   1·64   G. Falckenberg and Weight[5]
                    1·61   M. Jona.[6]

[5] G. Falckenberg & Weigt, Ann. d. Physik, 61, 2, p. 145, 1920.
[6] M. Jona, Phys. Zeits., 20, p. 14, 1919.

Ethyl Alcohol	1·64	G. Falckenberg and Weight.
	1·63	Krchma and Williams.[7]
n-Propyl Alcohol	1·66	G. Falckenberg and Weight.
n-Benzyl Alcohol	1·66	Williams[8]

It might here be incidentally mentioned that the value for electric moment obtained by Miss. L. Lauge[9] for the normal propyl alcohol is not very reliable. The value of the electric moment for this alcohol which is found by her to be equal to $1·53 \times 10^{-18}$ is at wide variance with the value of other observers.

It is also expected that the carbon atoms associated with the CH group forming the iso-alcohols should have different binding forces leading to different values of the electric moments. The results so far obtained by the different authors and also by the present authors support this statement. Experiments are also in progress to measure the electric moments of dihydric and polyhydric alcohols and also of secondary and tertiary alcohols. The results will soon be published in a separate paper.

The authors express their thanks to Mr. S. C. Sarkar for suggesting the measurement with the primary alcohols and also for helping us with some of his instruments and observations on primary octyl alcohol. Our gratefulness is also due to Prof. P. N. Ghosh for helpful criticism and continued interest during the progress of the work.

[7] Krchms & Williams, loc. cit.

[8] Williams, Phys. Zeits., 29, p. 204, 1928.

[9] L. Lange, Loc. cit.

X-Ray Absorption Limits and the Distribution of Electrons Round the Atom.

By

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During the last few years, the attention of the investigators in the X-ray region has largely been drawn to the precision measurements of both the emission lines and absorption edges, so as to be able to compute the energy values of the atomic levels as accurately as possible. In computing the values it is assumed after Kossel that the frequency of any emission line is the difference between the frequencies of the two levels in the atom and experiments justify this assumption in cases where direct verification is possible. In order to explain the absorption edges, Kossel assumed that inside the atom, the electrons are arranged in different levels each having a definite energy value. When a beam of X-rays passes through a large number of atoms, an electron from an inner electronic group is thrown entirely out of the atom by the absorption of energy from the primary radiation and the emergent beam when examined shows what is known as absorption line or edge. It was at first believed that the absorption edges are simple in structure but later works of Fricke,[1] Lindh,[2] and others have definitely shown that in compounds the primary absorption edge is well marked by

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[1] Phys. Rev., 16, 1920.
[2] Dissertation, Lund, 1922.

an absorption line followed by one or more regions of weaker and stronger absorption in the shorter wavelength side of the primary edge before the uniform continuous absorption is reached.[1] The possible appearance of this fine structure in the absorption edge was predicted by Kossel as being due to the fact that the electrons from any inner level might be removed to the outer optical levels, thus accounting for their frequency being lower than that at which the continuous absorption begins. While there is no doubt about the soundness of Kossel's interpretation about the fine structure of the absorption edge, it is generally believed that the " normal absorption edge " is formed when an electron from the inner group is thrown entirely out of the atom by the absorption of primary radiation. In view of the recent experiments especially from Siegbahn's laboratory, it seems that proper attention has not been paid to Kossel's theory about the process of absorption. It will be shown in this paper that Kossel's view is a very general one and is not confined to those atoms where fine structure of the absorption edge has been observed. Further it will be shown that purely absorption and emission data lend a general support to Saha Scheme of the distribution of electrons round the atom in preference to that of Main Smith and Stoner.

Absorption edges.

Kossel's view of the appearance of the successive maxima can be expressed as follows. The main K limit corresponds to the energy necessary to transfer an electron from the K shell to the periphery, and the secondary edges are due to the removal of an electron from the K shell to any one of the virtual optical level of the atom. The energy necessary for

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[1] In this paper a distinction has been made between the "secondary absorption limits" and "fine structure edge." The former is a general term and the latter is only a special case of the former in which the extreme limit of the fine structure edge, when expressed in volts, will not exceed the ionisation potential of the atom.

later transitions is necessarily higher than the true K limit and hence these edges lie on the shorter wavelength side and this is confirmed by experiments. It is suggested here that Kossel's view about the formation of the main K absorption limit is not only valid in atoms where fine structure of the absorption edges has been observed but also true for every absorption process.

It is well-known that one can compute the values of various energy levels in atoms from the precision measurements of emission lines and absorption edges, purely from X-ray data and in cases where the energy of the outermost shells is computed, it is found that these values come out to be either zero or considerably smaller than what would be expected from optical data. Thus the view that K edge, as ordinarily measured, does never correspond to the complete ionisation of the atom and the exact orbit where the inner electron will be removed will depend on the selection principle which governs the jumps between any two orbits and the intensity of these edges will primarily depend on the probability of such jumps. The question arises, what is the lowest peripherial level to which a K electron may be removed in the neutral atom. This point has thoroughly been discussed by Stoner.[1] When pure elements are examined, in general no fine structure is observed, it does not necessarily mean that they are non-existent but it may be they are not resolved by the spectrograph primarily due to the limited slit width which is generally taken as 0.1 mm. The degree of sharpness of these absorption lines is not so pronounced as in the optical spectra and moreover though there is a very sharp edge on the longer wavelength side, the other side presents a band-like structure. This can be clearly explained in accordance with the view expressed before. If the energy difference between two transitions of the electron from the K shell to the periphery of

[1] Stoner—Phil. Mag., Vol. II, July, 1926.

the atom and to the virtual optical level, expressed in wave-length, is sufficient, so as to be resolved by the spectrograph, the fine structure[1] will be observed. If the resolution of the instrument is not sufficient, the fine structure will be super-posed on the primary line on the shorter wavelength side and the whole structure will have an appearance on the band spectra with a very sharp edge on the longer frequency side. The same band-like structure appears itself in the measurements of absorption coefficient by ionisation chamber where the shorter frequency edge is very sharp while the other side shows a gradual fall till the normal absorption is reached. Recently Coster and Van der Tuuk[2] using very high resolving power have observed fine structure in the K absorption edge of Argon. They consider that this can be explained as due to transitions to different p levels since the separation of the two edges is about 1·7 volts which is about the same in the optical spec-tra. Experiments reveal the fact that not only the frequency of the absorption edges but also the emission lines of an atom change with different chemical combination of the same atom. From the absorption and emission measurements it is possible to compute the values of its various energy levels. One typi-cal example is given below[3] :—

	Sulphur Sulphate	Values of Difference
Sulphur		
K 181·85	182·68	0·83
LII 11·96	12·70	0·74
LIII 11·87	12·62	0·75

It will be observed from the above table, that the change in the absolute value of the K shell is greater than that of

[1]   Fricke—Phys. Rev., XVI, 1920.
       Siegbahn—Spectroscopy of X-rays.
[2]   Nature, 118, p. 586, 1926.
[3]   *Backlin, Zeit. f. Phys., Band 38.
       Ray—Phil. Mag., Vol. I, 1925.

the L shells in the sulphate compounds. At a first glance, it may appear curious that in the molecule, the innermost shell of an atom has undergone the greatest distortion or change. But according to the view expressed before, such a peculiar result is expected. It is well-known that peripherial electron or electrons play the part of binding two or more atoms in forming a molecule, and suffer the greatest distortion while such change is felt least by the inner shell so that when an electron from the K shell is transferred to the periphery one has to consider the effect of molecular force on both the K and the valency shell. While such a change is least in the K level the valency shell suffers the greatest distortion. But in the case L absorption edges the L levels are more affected than the K level by its promixity to the other atoms forming the compound and thus the total energy change in the K edge in compounds appears greater than that of the L levels.

Absorption edges in compounds.

Extensive investigation has been done by Lindh[1] on the main absorption edge and its fine structure for a large number of element of lower atomic number where he observes that the shorter wavelength side of the main K limit is accompanied by one or more edges. The energy difference of the secondary edges from the main one remains practically the same for different compounds where the element investigated has the same valency. Similar fine structure has also been observed in L absorptions for elements with higher atomic number. Though no satisfactory solution has yet been offered to this remarkable process, a simple explanation suggests itself in accordance with the former view. It will be also assumed here that by the absorption of radiation, any electron from

[1] Dissertation, Lund, 1923.

the K shell of an atom forming a compound may either be transferred to the periphery of the molecule or to any virtual orbit (if any) or to the boundary of the molecule (zero energy of the electron). In such a case if we examine the fine structure of the absorption edge of one of its atoms forming the molecule we should expect the main K limit and extreme K limit of the atom in the molecule will be separated by a few volts which ought to be the same as the ionisation potential of the molecule itself. The same separation would be expected of the other atom in the molecule. Thus the separation between the K_1 and K_2 of chlorine in $MgCl_2$ is 14·0 volts (chlorine is here monovalent) while the ionisation potential of the molecule is 12·6 volts But there are molecules we have to deal with where it is very difficult to say that the molecule has a definite ionisation potential. In such cases though the separation between the two K edges cannot be compared with the ionisation potential of the compound in question, yet it is interesting to note that this separation is the same in different elements of the compound itself. This expectation has been found to be fulfilled by the' recent experiment of Nuttall.[1] In the case of a simple compound like KCl, Nuttall observes several secondary absorption edges for both the potassium and chlorine atom which he designates as A, B, C, D, etc. The first absorption edge is A. He finds that the difference between A and B for Potassium atom in KCl is 4·9 volts; the difference between the corresponding two edges in chlorine for the same compound is 4·0 volts. Incidentally it may be remarked that Franck, Kuhn and Rollefson[2] have found the dissociation energy of the molecule to be 4·5 volts by spectroscopic observation.

In view of the difficulty in the measurements of the edges and also due to the uncertainty about the exact position

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[1] Phys. Rev., 31. 1927.
[2] Zeit. f. Physik, Band, 43,

taken up by the electron by the absorption of radiation this agreement is surprising.

In examining the shift of the K edge from the free element to compounds of the same element a simple relation comes out of itself. Following Lindh, K will be designated as the primary absorption edge for corresponding to that of the " free element" and $K_2 K_3$ etc., denote corresponding edges of the fine structure edges, it is found that in different elements of a compound of similar structure, the separation of the K edge in the elementary atom from that of corresponding edge of the same atoms in the compound is practically the same.

The following are the typical examples of the above statement :—

Element.	Difference between K_1 and K_2 in volts.
Cr Cr_2O_3	13·0 volts
Fe Fe_2O_3	13·0 volts
Ti TiO_2	17·0 volts
Mn MnO_2	15·6 volts
Fe $FeSO_4$	9·1 volts
S $FeSO_4$	10·1 volts
Mn $MnSO_4$	9·7 volts

Though no theoretical explanation can be given to the above relation unless more compounds of similar structure

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have been thoroughly examined yet this simple relation seems to be striking.

In some cases this simple relation will not be true. The reason for such a departure is due to the fact that in compounds of the type HCl, the H^+ penetrates inside the chlorine shells and thus influences all the inner levels.

So far the simple secondary absorption limit can be explained by Kossel's view but recent experiments of Nuttall (*loc. cit*) raises the serious question whether all the edges he has observed could at all be explained on this view. He observes five absorption edges in chlorine and potassium atoms in the simple compound KCl where both the potassium and chlorine atoms are monovalent. The extreme limit of the absorption edge from the primary edge is 27·3 volts for chlorine and 67·4 volts for potassium, that it raises a broad issue, how far the question of valency and multiple ionisation theory of the atom is responsible for this tremendous shift. This aspect of the problem will be treated in a separate paper.

Arrangement of electrons in the atoms.

Recently two rival theories about the electronic structure of atoms have been built up on the basis of Bohr model. The difference between two schemes is as follows: In one scheme (Stoner and Main Smith) L levels are divided into three and M levels in five sub-groups, etc., while according to the other scheme, mainly due to Saha (based on the works of Russel, Pauli and Hund) the division of each of the L_2, M_2, N_2, etc., into two sub-groups is more apparent than real, and two sub-levels L_{21} and L_{22} ought to be united under one single L_2 level instead of being split up. Stoner's Scheme has sometimes given rise to certain misconceptions. Some investigators assume that when the M_3 level is filled up, as for example in the transitional groups, either of the M_{32} or M_{33} sub-levels is first filled up to its maximum number of electrons and then the

other level begins to be filled up. Saha and Ray (Phys. Zeit., 1927, 28, 221) have shown that this conception is opposed to the actual structure of outer shells as revealed by analysis of optical spectra, to account for which we have to assume that the electrons are not divided into two statically distinct sub-levels, but only in one M_2 or M_3 level.

Recently this view has been worked out by Ghosh[1] on the idea that the ionisation potential of a particular element rises gradually with the number of electrons in the outermost shell, i.e., the ionisation potential reaches the maximum value when the outer shell is completed. From the gradual rise and sudden breaks of the ionisation potential of the element from Hydrogen to Germanium, Ghosh gives a general support to the Saha Scheme of the atom that there is short period of 2 (corresponding to the formation of alkalies), a period of 6 (corresponding to the formation of regular group of elements, ending in each case in an inert gas) corresponding to the filling up of X levels, and so on.

According to the view expressed here that in the actual absorption process the electron from any shell (say K edge) is not transferred from this shell to infinity but is lifted either to the periphery of the atom or to any virtual optical orbit. If the view is accepted, then as the binding of the valency electron or ionisation potential of the elements shows regular and systematic variation, one would expect the same shape or similar change in the K absorption measurement. The energy of the innermost shell (K shell) should only follow regular increase from the lighter to the heavier atom. But the change of the actual K limit due to the variation of the ionisation potential of the elements alone is so small that a curve with $\sqrt{\frac{v}{R}}$ for K limit and the atomic number will be a simple straight line. In order to detect any change in the K limit a curve with $\Delta\frac{v}{R} = K - K\beta_1$ (where K and $K\beta_1$ denote

[1] Journal of Chemical Soc., Vol. IV, 1927.

the value of $\frac{v}{R}$ for absorption limit and $K\beta_1$ emission line respectively) and atomic number is drawn so that the discontinuity may clearly be brought forward and gradual rise and sudden changes are at once noticed similar to that obtained by Ghosh & Saha (l.c.). The reason for choosing the $K\beta_1$ line is due to the fact that the frequency of this line is very nearly equal to that of the K limit in the region covered in the graph and also the line $K\beta_1$ changes continuously from Magnesium (N = 12) upwards as has been clearly shown by Siegbahn in the "semi optical lines in X-rays."[1]
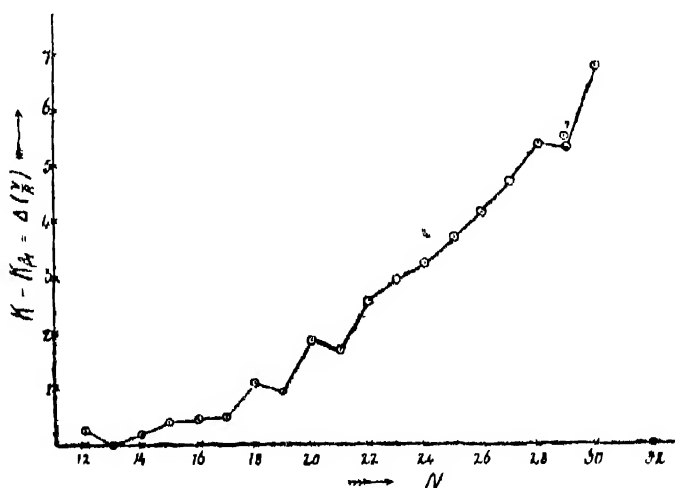
Fig. 1.

From the curve it is clear that there is a fall in Aluminium (N = 13) after which it rises till Argon. The curve slopes again at potassium (N = 19) only to rise again at Calcium (N = 20) after which there is another fall at Scandium (N = 21). The curve then gradually rises till Nickel (N = 28). The kink appears at copper (N = 29) and increases again at Zinc (N = 30). No attempt is made to extend the curve beyond zinc, as the relative change in $\triangle\frac{v}{R}$ gradually gets higher

[1] Phil Mag., Feb., 1925.

and higher and no such small changes could be detected.[1] In the above curve the values of $\frac{v}{R}$ for the K absorption edges are taken from Ase, which are the most recent values from Siegbahn's laboratory and also from Lindh (l.c.). The Argon $K\beta_1$ line is interpolated following Moseley's law in this region. Scandiun ($N=21$) K absorption was measured by Fricke in 1920, whose results show systematic variation from the more precision measurements now employed in Siegbahn's laboratory. The K limit for Scandium is computed from Walter's values of absorption measurements.

It is surprising that the form and nature of the curve in this region is similar to that obtained by Ghosh although such abrupt and high variation could not be observed here. This is what would be expected from the standpoint taken in this paper about the absorption process in general in X-rays and also supports the Saha Scheme of the electronic structure of the element in preference to that of Main Smith and Stoner.

Summary and conclusion.

Kossel's view of the absorption process and the fine structure lines is developed in this paper especially to explain the secondary edges in compounds, and a general relation is found that in different elements of a compound of similar structure the separation of the K edge in the elementary atoms from that corresponding edge of the same atoms in the compound is the same. Some examples are given in support of the above rule, and the cases of failure of this general rule are discussed.

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[1] In the region of the first transition group, if a similar curve is drawn with $\triangle\frac{v}{R}=K-K\beta_2$ (Siegbahn's notation), it is found that it gradually rises till Nickel and after which there is a fall at copper only to rise again at zinc. The curve is not so smooth as the one drawn in the paper. But the slope at copper comes out prominently.

The discontinuities in the curve with $\Delta \frac{v}{R} = K - K\beta_1$, and atomic number from aluminium to zinc lends a general support to the Saha Scheme of the electronic distribution of an atom and suggest that Main Smith and Stoner's Scheme might be more apparent than real.

My thanks are due to Prof. D. M. Bose and Prof. P. N. Ghosh for helping me in the discussion of the subject in the course of writing the manuscript.

UNIVERSITY COLLEGE OF SCIENCE,

92, UPPER CIRCULAR ROAD,
CALCUTTA.

A Note on the Structure of Atomic Nuclei.

By

M. F. Soonawala, M.Sc.

As is well known, the periodicities in properties, physical and chemical, of elements has received ample attention as in the classical work of Mendeleeff, and more recently of Bohr, Main Smith and Stoner in particular. Of late, however, the problem of the building up of the atomic nuclei themselves has come to the fore ; as for example in Millikan's work on the Cosmic Rays, and the several researches on the internal constitution of the stars. Millikan believes the source of the cosmic says to be the synthesis of protons and electrons in the interstellar space ; and this has naturally suggested the pertinent query,—"Why the most favoured condensation of protons and electrons should be those which go to build up the few nuclei which are actually found to constitute the greater part of ponderable matter." This note is believed to lead us a step forward in answering this query.

The Table set out below is constructed on the hypothesis that atomic nuclei are formed by the synthesis of protons, electrons and rare gas nuclei. The combinations of two positively charged nuclei and one or more electrons is represented in the Table, the effect of additions of electrons being to change the atomic number without materially affecting the atomic weights of the isotopes of the elements. The values of the isotopes are those given by

Aston.[1] We may presume that further investigation will reveal the existence of more isotopes of some of the elements. In the meantime, the Table brings out some broad features, which arrest our attention.

The following are the salient facts arising as a natural consequence of the arrangement given :—

1. The halogens, the alkali metals, and alkaline earths show similarities in their respective origins, as seen on inspecting the horizontal rows showing combinations of protons and He nuclei with the nuclei of rare gases.

2. The combinations of the isotopes of A and Ne yield nuclei of atomic weights ranging between 56 and 62, and atomic numbers 28 and less. This coincides with the group Fe, Ni, Co, the atomic weights of whose isotopes lie between 54 and 60, and whose atomic numbers are 26, 27, and 28 respectively.

3. The combinations of Ne and Kr isotopes give a possible range of atomic weights between 98 and 108, and of atomic numbers 46 and less. This falls in with the group Ru, Rh, Pd, whose isotopes range in atomic weights between 101 (or a little less) and 107 (or a little more), and whose atomic numbers are 44, 45, and 46 respectively.

4. The combinations of the isotopes of X and Ne yield isotopes of atomic weights from 144 to 158 of elements of atomic numbers 64 and less. This fits in with the occurrence of the rare earths from La (at. wt., 139 : at. no. 57) to Gd. (at. wt. 157. 3 ; at. no. 64).

5. The combinations of the isotopes of A and Kr give several of the isotopes of Sn and Cd. The possible range of atomic weights is from 114 to 126, while for Sn and Cd there are 17 isotopes having atomic weights between 110 and 124. The maximum atomic number allowed is 54, while the atomic numbers of Sn and Cd are 50 and 48

[1] Phil. Mag., 49, 294, p. 1198 ; and Nature, 31 Dec., 1927, 958.

respectively. In this connection it is noteworthy that Aston observed a marked similarity between the mass-spectra of these elements.[1]

6. Combinations of A and X isotopes would result in elements having weights between 160 and 176 and of atomic numbers 72 and less. This fits in with the group of rare earth elements lying between Tb. (at. wt. 159.2, at. no. 65) and Lu (at. wt. 175, at. no. 71).

7. The combinations of the isotopes of Kr amongst themselves would once again give the rare earths from Tb to Lu ; but, when we see the failure of the occurrence of isotopes of atomic weights 2, 8, and of Ca^{41} we can doubt if two similar nuclei can at all combine together. In that case, the Kr-Kr combinations should also fail.

8. The combinations of the isotopes of Kr and X take us into the midst of the radioactive elements. Here a complication arises in that these elements can also result from the disintegration of heavier nuclei.

9. The recent discovery of the isotope Ne^{21} is noteworthy[2] as with one, two, and three nuclei of He, Ne will yield the isotopes Mg^{24}, Mg^{25}, Mg^{26}, Si^{28}, Si^{29}, Si^{30}, S^{32}, S^{33}, S^{34}.

10. Naturally, the number of the parent nuclei, those of the rare gases, may be expected to be heavily depleted, as has been remarked in the case of the rare gases.[3]

11. Proceeding horizontally along a row, or vertically down a column of the table, the elements most probably fall in the order of diminishing frequency of occurrence.

[1] Phil. Mag., l.c., p. 1196.

[2] Hogness and Kvalnes, Nature, 22nd Sept., 1928, p. 414.

[3] Aston, Nature, Nov. 29th, 1924.

MAHARAJA'S COLLEGE,
    JAIPUR :
The 3rd January, 1929.

Table to show formations of atomic Nuclei from Rare Gas Synthesis.

	1	4	20	21	22	36	40	78	80	82	83	84	86	124	126	128	129	130	131	132	134	136	222
H	H	He	...	...	...																		
He	O	O	Mg	Mg	Mg	Cl	K	Br	Br	...	...	Rb	Rb	O	I	...	Te	...	...	Cs	...	...	Rn
Ne	O	O	Mg	O	Na	Ca	Ca	Se	...	Sr	Rb	Sr	Zr	Te	Te	...	Cs	...	...	...	Ba	Ba | Ce	1
A		O	Ca	O	O	O	—																Ba
Kr					Ca																		

X (row, at wt. 130) — *Rn* (row, at wt. 222)

Ne (at. wts. ~36–86):
Possible at. wts. from 56 to 62. Possible at no. 28 Fe, Ni, Co; Group at. wts. 54 to 60 at. nos. 26, 27, 28.
Ca.

A (at. wts. 78–108):
Possible atomic weights: from 98 to 108. Possible atomic numbers: 46 and less.
Group Ru, Rh, Pd, At. wts. from 101·7 to 106·7 At. nos. 44, 45 and 46
Ge, Se.

X / Ne (Rare Earths, 124–158):
Of Rare Earths, La to Gd.

		Possible
At. wts.	144 to 158	139 to 157·3
At. nos.	64 and less	57 to 64

Kr (at. wts. 114–175):
Possible at. wts. 114 to 126.
„ at. Nos. 54 and less.
Sn and Cd. At. wts. 110 to 124
At. nos. 50 and 48

Possible Of Rare Earths Tb Lu
At. wts. 156–172   159·2 to 175
At. nos. 72 & less   65 to 71

(Rare Earths Tb to Lu, 159–176):
Of Rare Earths (Tb to Lu)

		Possible
At. wts.	160 to 176	159·2 to 175·0
At. nos.	72 and less	65 to 71

Rn (Radioactive Elements):
Of Radioactive Elements

		Possible
At. wts.	202 to 222	206 to 238
At. nos.	90 and less	82 to 92

Unstable elements.

← Unstable elements →

Note on Wien's Displacement Law and Radiation Pressure from the Light Quantum Hypothesis.

By

Bishwambhar Nath Srivastava, M.Sc.

and

Daulat Singh Kothari, M.Sc.

It was Planck who first suggested the hypothesis of radiation quanta. This has been successfully applied for the tackling of problems in all branches of physics. Einstein applied the idea to explain photo-electric effect, Ehrenfest discussed its application to heat radiation, Saha explained the pressure of light on atoms on this hypothesis, and A.H. Compton has applied it to X-ray scattering. In this note we shall try to prove that Wien's Law and the magnitude of radiation pressure can be very easily proved with the hypothesis of light quanta.

§ 1.

Doppler Effect in deducing Wien's Law.

In the deduction of Wien's Displacement law, we start with the conception of an enclosure with perfectly reflecting walls containing radiation. The walls of the enclosure are then supposed to expand out normally, thus bringing about a change in the wave-length of the radiation as it is incident on the walls of the enclosure (due to Doppler effect).

We shall calculate this change of wave-length on the hypothesis of quanta.

$$S \begin{array}{c} \downarrow \\ \hline \end{array} \begin{array}{c} v \\ \longrightarrow \end{array} \quad \begin{array}{c} hv \\ \longleftarrow \\ c \end{array}$$
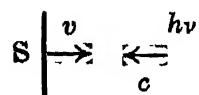
Let n be the number of quanta per c.c. in the incident radiation. If the mirror S be at rest, it will receive $n \times c$ quanta per unit area of its surface per sec. If it moves towards the light with velocity v as indicated in the Fig. the number of quanta striking it per sec. becomes $n(v+c)$.

Let the initial frequency of the radiation be ν and the frequency after reflection ν'.

Therefore, change in momentum suffered by a quantum

$$= \frac{h\nu}{c} + \frac{h\nu'}{c}.$$

Hence the pressure exerted by the incident quanta on the moving mirror = change in momentum suffered by the quanta per sec.

$$= p = \frac{h}{c}(\nu + \nu') \, n \, (v+c).$$

Therefore, the work done per second by the moving mirror, i.e., energy imparted to the $n(v+c)$ quanta

$$= pv = \frac{h}{c}(\nu + \nu')(v+c) \, nv.$$

Hence the energy imparted to each quantum

$$= \frac{h}{c}(\nu + \nu')v \qquad \ldots \qquad \ldots \qquad \ldots \quad (1)$$

The gain in energy by a quantum on reflection

$$= h(\nu' - \nu) \qquad \ldots \qquad \ldots \qquad \ldots \quad (2)$$

Equating (1) and (2),

$$h\,(\nu' - \nu) = \frac{h}{c}\,(\nu + \nu')\,v$$

or
$$\frac{\nu'}{\nu} = \frac{c+v}{c-v} = \frac{\lambda}{\lambda'}$$

or
$$\Delta\nu = \frac{2v}{c-v}\,\nu = \frac{2v}{c}\,\nu \quad \text{approx.} \qquad \dots \qquad \dots \quad (3)$$

the same result as is derived on the wave theory.

With the help of this result Wien's displacement law can be easily deduced and the method of deduction will be found in most text-books.

§ 2.

PRESSURE EXERTED BY RADIATION ON A MOVING REFLECTOR.

Larmor gave for the pressure exerted by radiation on a moving reflector the expression

$$P = \frac{c^2 - v^2}{c^2 + v^2}\,[E + E'],$$

where E, E' represent the energy density in the incident and the reflected radiation respectively, c the velocity of light and v the velocity of the reflector towards the incident radiation. He deduced this expression from consideration of electromagnetic waves. Here it is deduced on the light quantum hypothesis.

Let the frequency of the incident radiation be ν. Each incident quantum has energy $h\nu$ and momentum $\frac{h\nu}{c}$. Due to the motion of the reflector the frequency associated with

the reflected quantum becomes ν' such that $\nu' = \nu + \dfrac{2v}{c-v}\,\nu$ [See eqn. 3]. Therefore change of momentum suffered by a quantum on striking the mirror

$$= \frac{h\nu}{c} + \frac{h\nu'}{c}$$

$$= \frac{2h\nu}{c-v} \quad \dots \qquad \dots \qquad \dots \qquad \dots \quad (4)$$

The number of quanta striking the reflector per second $= n\,(v+c)$ where n is the density of quanta in the incident radiation. Therefore, total change of momentum per second per unit area = pressure exerted on the reflector

$$= p = \frac{2h\nu}{c-v}\,(c+v)\,n \qquad \dots \qquad \dots \qquad \dots \quad (5)$$

Again the energy density in the incident radiation $E = nh\nu$. Also $E' = n'h\nu'$ where n' denotes the density of quanta in the reflected radiation. We have to calculate n'. It has been shown above that the number of quanta striking the reflector per second is $n_1 = n\,(v+c)$.

Hence the number of quanta leaving the mirror per second is also n_1. Consider all the quanta reflected from the mirror in a second. Those of them leaving the reflector earliest will at the end of a second be at a distance c from the initial position of the reflector or at a distance $(c-v)$ from its final position. Thus all these n_1 quanta would be enclosed in the space $(c-v)$ and hence the density of reflected quanta becomes,

$$n' = \frac{n_1}{c-v} = \frac{c+v}{c-v}\,n$$

$$\therefore \quad \frac{n'}{n} = \frac{c+v}{c-v} \qquad \dots \qquad \dots \qquad \dots \quad (6)$$

Hence $\qquad$ $E' = n'h\nu'$

$$= nh\nu \left[\frac{c+v}{c-v}\right]^2 \text{ from (3) and (6)}$$

$\therefore \qquad E + E' = nh\nu \left[1 + \left(\frac{c+v}{c-v}\right)^2\right]$

$$= 2nh\nu \cdot \frac{c^2 + v^2}{(c-v)^2} \quad \dots \qquad \dots \qquad \dots \quad (7)$$

Now from (5)

$$p = 2nh\nu \cdot \frac{c+v}{c-v}$$

$$= \frac{c^2 - v^2}{c^2 + v^2} [E + E']$$

which is exactly the same expression as deduced by Larmor from considerations of electromagnetic waves.

Putting $v = 0$, we obtain

$$P = (E + E')$$

a theorem which is well-known.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF ALLAHABAD :
November 20, 1928.

On an Easy Proof of the Formula for Cumulative Grid Rectification.

By

Daulat Singh Kothari, M.Sc.

For the detection of wireless waves, a triode valve may be employed in either of the three well-known ways:

- (*i*)   Anode current rectification.
- (*ii*) Cumulative grid rectification.
- (*iii*) Heterodyne reception.

The derivation of the formula for the rectified current in the case (*ii*) is rather difficult when compared to the other two cases. The method of proof usually given in text-books ignores or rather does not clearly bring in evidence the action of the grid condenser.[1,2]

Fig. 1 represents the circuit for this method of reception as ordinarily used and Fig. 2 represents the

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[1]   L. B. Turner,   Wireless Telegraphy and Telephony (1921),   p. 116.
[2]   J. H. Morecroft,   Principles of Radio Communication (1927), p. 535.

equivalent circuit diagram.　The notation is clear from the Figures 1 and 2.
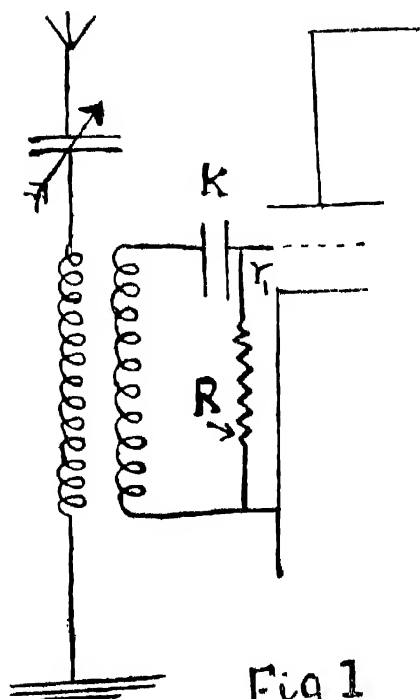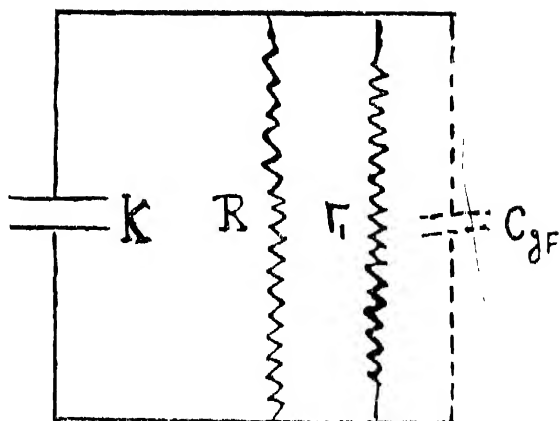
Fig. 1　　　　Fig. 2

Because of the non-symmetrical conductivity of the path shunting the condenser K, charge will accumulate on it, till a state of equilibrium is reached, i.e., the condenser receiving as much charge in time Δt, as it loses in time Δt by discharging through the resistances.

Let E be its P. D. when the steady state is reached.

The rectified current in the grid filament circuit

$$-\frac{e^2}{4}\frac{d^2 I_g}{dE_g^2}$$

where the impressed signal is $e \sin pt$.

Charge accumulating on the condenser in the time Δt

$$-\frac{e^2}{4}\frac{d^2 I_t}{dE_q^2}\,\Delta t.$$

Again

$$E' = Ee^{-\dfrac{t}{\dfrac{K.\,R\gamma_1}{R + \gamma_1}}}.$$

Equation of discharge of the Condenser.

R is the leak resistance and,

r_1 is the grid-filament resistance.

C_{gF} is the grid-filament capacity,

$$\triangle E' = \dfrac{E}{K\dfrac{R\gamma_1}{R + \gamma_1}} \triangle t$$

∴ Charge lost in time $\triangle t$

$$= \dfrac{E}{K\dfrac{R\gamma_1}{R + \gamma_1}} K \triangle t$$

$$= \dfrac{e^2}{4} \cdot \dfrac{d^2 I_g}{dE_g^2} \cdot \triangle t$$

$$\therefore \quad E = \dfrac{\dfrac{e^2}{4}\dfrac{d^2 I_g}{dE_g^2}}{\dfrac{1}{R} + \dfrac{1}{\gamma_1}}$$

But

$$\dfrac{1}{\gamma_1} = \dfrac{dI_g}{dE_g}$$

$$\therefore \quad E = \dfrac{\dfrac{e^2}{4}\dfrac{d^2 I_g}{dE_g^2}}{\dfrac{1}{R} + \dfrac{dI_g}{dE_g}}$$

earlier method. Whereas we had to expose about 70 to 80 hours, or even more to get a good photograph in the first way we could get a good photograph in about an hour by Wood's method.

We have used a Hilger Constant deviation Spectrograph and a Cooper Hewitt lamp of approximately 2000 C. P. The spectrograms are reproduced in Plate No. xxii. Fig. 1 is the spectrogram of the incident mercury arc, (2) that of the magnesium sulphate, (3) that of sodium sulphate, (4) that of copper sulphate, the spectrogram of aluminium sulphate being too faint to be reproduced, (5) that of the sulphuric acid. The measurements of the wavelengths were made by means of Hartmann dispersion formula and are given in Table No. 1. In the case of the sulphates investigated there are only two modified lines one at 4552·2 A. U. excited by 4358·34 and the other at 4213·7 A. U. excited by 4046·56, wave-number difference between the excited and the exciting lines being 977 and 980 (*vide* Table 2) corresponding to infra-red absorption at $10·2\mu$. Coblentz' data for the infra-red absorption of the sulphates show edges of absorption at $9·2\mu$, but the calculated infra-red absorption band lies here at $10·2\mu$ In the case of sulphuric acid there are five modified lines on a continuous back ground. The infra-red absorption data of Coblentz as determined from reflection show the absorption bands lying at $8·6\mu$, $9·55\mu$, $10·4\mu$, $11·35\mu$. The calculated absorption bands at $11·01\mu$ and $10·96\mu$ correspond to Coblentz' value at $11·35\mu$ while the others, *viz.*, $17·9\mu$, $18·4\mu$, $4·68\mu$ together with Coblentz' value at $9·55\mu$ seem to indicate that 18μ is the fundamental and $9·55\mu$ and 4.68μ are the overtones (*vide* Table 2). In case of the sulphates the two characteristic water bands always appear corresponding to the infra-red absorption band at 3μ.

It is interesting to note that in each of the solutions investigated we have got always the same frequency for the scattered components. We are inclined to consider this

—5461   —4916   —4358   —4078
                                                           —4046
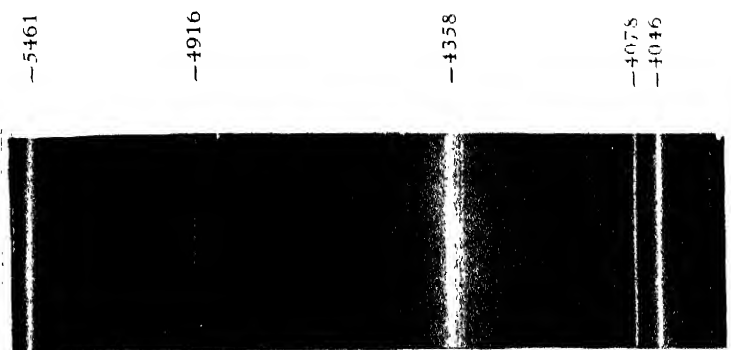
Fig. 1.
Hg
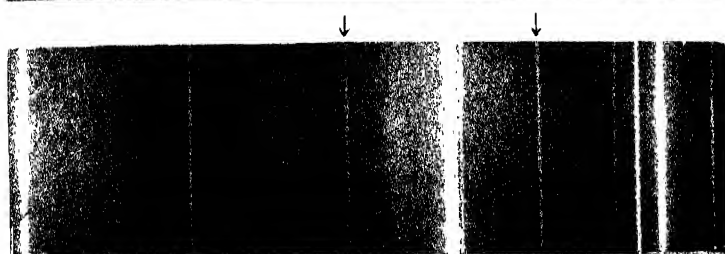
Fig. 2.
MgSO₄
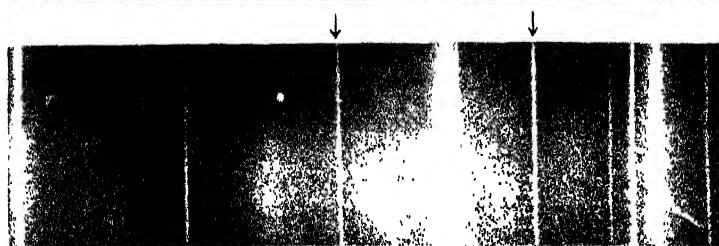
Fig. 3.
Na₂SO₄
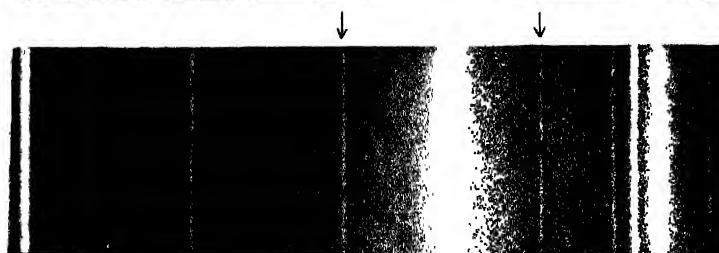
Fig 4.
CuSO₄

Fig. 5.
H₂SO₄

RAMAN SPECTRA
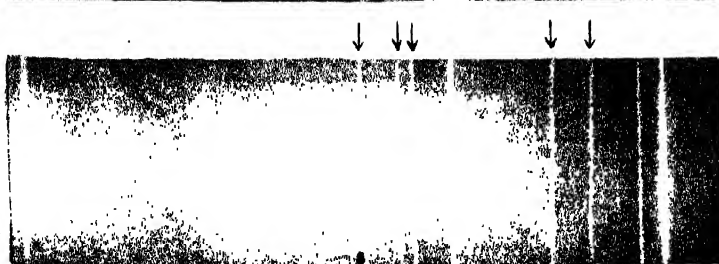
infra-red frequency as due to the SO_4-ion. The absence of any specific effect of the kation may be regarded incidentally as justifying the hypothesis of complete dissociation of strong electrolytes, as postulated by Ghosh.

The investigation of other salts, as well as the specific effect of the solvents is in progress.

In conclusion we wish to express our thanks to Prof. S. N. Bose, Dacca University, for having suggested the problem and for helpful guidance and the keen interest he took during the progress of the work.

TABLE 1.

Substance	Modified Line		Exciting Line		Wave no. Diff.
	Wavelength (air) in I. A.	Wave no. (Vac.)	Wavelength (air) in I. A.	Wave no (Vac.)	
H_2SO_4	4537·9	22030	4358·3	22938	908
	4464·0	22395	4358·3	22938	543
	4482·5	22554	4046·5	24705	2151
	4202·7	23793	4046·5	24705	912
	4140·2	24147	4046·5	24705	558
Sulphates.					
$MgSO_4$ Na_2SO_4 etc. }	4552·2	21961	4358·3	22938	977
	4213·7	23725	4046·5	24705	980

TABLE No. 2.

	Wave no. shift	Calculated wavelength in μ	Coblentz' values in μ
H_2SO_4	908 } 912 }	11·01 } 10·96 }	11·35
	543 } 558 }	18·40 } 17·99 }	9·55
	2151	4·65	
Sulphates	977		
	980	10·2	9·2

–

X-Ray Diffraction in Liquids and Solutions and the Molecular Structure Factor.

By

P. Krishnamurti.

(Plates XXIII and XXIV.)

Abstract.

In continuation of his previous work on X-ray diffraction by pure liquids and solutions, the author has now examined substances consisting of symmetrical molecules, both in the liquid state and in solutions of different concentrations.

Tetranitromethane which crystallises in the cubic system gave two rings for the liquid having the spacings 5·49 and 3·02 A.U. respectively, whereas in *a dilute solution* in benzene or cyclohexane, a strong scattering at small angles and a faint maximum at 3·02 A.U. were observed. It is shown that the strong inner ring in the liquid is due to diffraction by neighbouring molecules and hence is intermolecular, while the faint outer ring is due to the structure factor of the molecule and hence is intramolecular. A study of dilute solutions is shown to be of value in determining the structure factor of the molecule.

Aqueous solutions of *hexamethylene tetramine*, a substance crystallising in the body-centred cubic system have also been studied. In a concentrated solution, a broad inner maximum and an outer one at 2·86 A.U. were observed. But in more dilute solutions, the water ring was superimposed upon the latter, shifting its position to smaller angles.

Dilute solutions of *carbon tetrachloride* in cyclohexane gave faint outer maxima in approximately the same position as in the pure liquid. This supports the view that the outer ring of the liquid owes its origin to the molecular structure factor.

It is suggested that since the spacings of the liquid haloes are calculated according to the Bragg formula, it is not the distance between neighbouring molecules but the distance between the planes containing the maximum number of molecules per unit area which should be considered, and these planes occur in the liquid approximately as they do in the crystal. In the case of a simple cubic array considered by Raman and Ramanathan it has the value $1{\cdot}00 \times n^{-\frac{1}{3}}$, but in other cases it has different values, as in the body-centred cubic $(0{\cdot}97n^{-\frac{1}{3}})$ and face-centred cubic $(0{\cdot}92n^{-\frac{1}{3}})$ arrangements.

The use of hexamethylene tetramine powder for standardising an X-ray camera when using soft radiation is also pointed out.

1. Introduction.

In the previous work on solutions carried out in this laboratory,[1,2] the author came to some general conclusions regarding the state of the dissolved molecules in aqueous and non-aqueous solutions. In dilute aqueous solutions, various substances like ammonium nitrate, acetamide, cane sugar and levulose gave patterns which showed an intense scattering at small angles to the primary beam, the extent of which depended on the size of the dissolved molecule, large molecules giving rise to smaller but more intense diffraction disks. This phenomenon was interpreted as due to diffraction by the molecules of the solute distributed at random in the solution. The further interesting fact was also observed that when the concentration of the solution was increased, the scattering at small angles diminished and a new maximum at larger angles was observed. The patterns for the most concentrated solutions resembled those of the solutes in the liquid or solid states. In all these experiments the solute molecules were highly unsymmetrical so that the substances did not

[1]   Krishnamurti, Ind. J. Phys., 2, iv, 501 (communicated, 18th June, 1928).
[2]   ,,   ,,   3, ii, 209 (communicated, 15th October, 1928).
       Also J. A. Prins, Nature, January 19, 1929.

crystallise in any system possessing a high degree of symmetry. The occurrence of the lattter type of substances in the organic world is very limited indeed, but a study of such cases is of fundamental importance, and would no doubt lead to a correct interpretation of the origin of the diffraction haloes for liquids, which is at present not clear. According to the views put forward by Raman and Ramanathan [1] as early as 1923, the X-ray pattern of any liquid is due to its molecules acting as diffracting centres, the size of the halo being determined by the distance between neighbouring molecules. Most of the work carried out in this laboratory [2,3,4] go to support this view. There has however been a tendency to assume a kind of aggregation of the molecules in the liquid, and termed by G. W. Stewart as 'cybotaxis.' [5] The rough similarity of the patterns of many organic substances in the solid and liquid states [6] seems to agree with this view. The present experiments however indicate that the former explanation is likely to be a more general one in the case of liquids.

The best type of a symmetrical molecule would be methane or carbon tetrachloride, both of which crystallise in the regular system. The latter has been studied in the liquid state by Wyckoff [7] and in greater detail by Sogani, [8] who obtained two rings of which the inner one was strong and sharp while the outer one was faint and diffuse. He was inclined to view the fainter ring as a second order of the first, though he did not exclude the possibility of its being a purely molecular effect.

[1] Raman and Ramanathan, Proc. Ind. Ass. Cult. Sci., 8, 127 (1923).
[2] Sogani, Ind. J. Phys., 1, iv, 357 (1927).
[3]   „   „   2, i, 97 (1927).
[4] Krishnamurti, Ind J. Phys., 3. ii, 225 (1928).
[5] Stewart and Morrow, Phys. Rev., 30, 232 (1927).
[6] Herzog and Janeke, Z. f. Phys., 45, 194 (1927).
[7] Wyckoff, Am. J. Sci., 5, 455 (1923).
[8] Sogani. Ind. J. Phys., 2, iii, 377 (1928).

The difficulty of working with a strongly absorbing liquid like carbon tetrachloride using the copper radiation is obvious. Hence a search was made for a suitable liquid and tetranitromethane was finally selected for this work. This substance has been examined by Mark and Noethling [1] and found to belong to the cubic system. The molecule is nonpolar, possessing a dielectric constant of only 2·1. It was examined in the liquid state and in solutions of different concentrations both in benzene and cyclohexane.

Another substance crystallising in the cubic system and whose crystalline structure is fully known is hexamethylene tetramine $C_6H_{12}N_4$, whose molecules are also nonpolar. As this substance melts at a very high temperature (280°C), it was not examined in the liquid state, but its aqueous solutions of varying concentrations were examined. Incidentally, it may be pointed out that this substance hexamethylene tetramine or urotropin can be used as a standard substance for fixing the positions of the lines when using the powder method and the soft radiations of copper, iron or chromium.

2.   Results.

Tetranitromethane :—The liquid gave a pattern very similar to that of carbon tetrachloride. The inner ring was very sharp while the outer one was faint and diffuse. There was some general scattering within the inner ring, but the space between the two rings was quite clear. Outside the second ring some general scattering was also observed. The spacings of the two rings were 5·49 and 3·02 A.U. respectively.

Tetranitromethane-Benzene Solutions :—Benzene gave an intense ring with some amount of scattering extending to a small region outside the halo. A 1 : 3 solution (by weight) of tetranitromethane showed a strong scattering at small angles

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[1]   Mark and Noethling, Z. f. Krist., 65, 435 (1927).

TETRA NITROMETHANE
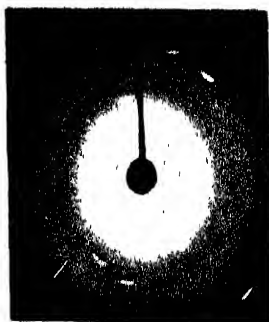
CYCLOHEX. SOLN. 1:2
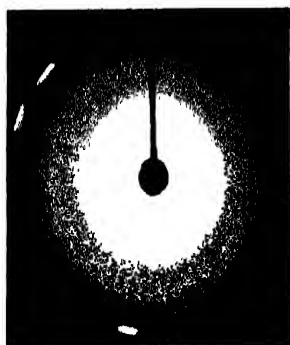
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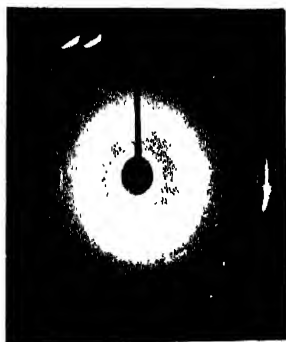
CYCLOHEX·SOLN, 1:4
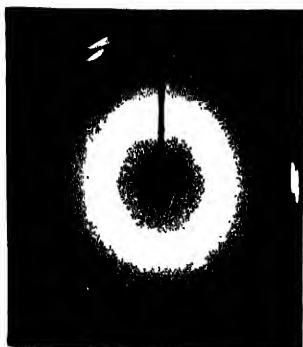
BENZENE
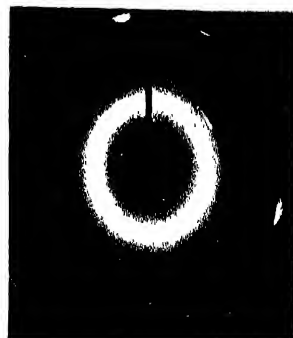
CYCLOHEXANE

X-RAY DIFFRACTION IN SOLUTIONS

which diminished gradually till the benzene ring was reached. Outside the latter, another faint maximum was also observed which was however very diffuse. This maximum was almost in the same position as the outer ring in liquid tetranitromethane. In a more concentrated solution (about 1 : 1 by weight) the scattering at small angles became very much stronger and extended up to the benzene ring. The outer maximum became stronger and more distinct, though it remained in approximately the same position as before.

Tetranitromethane-Cyclohexane Solutions :—Cyclohexane, unlike benzene, did not give any appreciable amount of scattering outside its principal halo, and was hence considered suitable for examining the effects expected in that region. A very dilute solution (1 : 6 by weight) showed a strong scattering at small angles, and also a perceptible maximum at a larger angle just outside the cyclohexane ring, in about the same position as the outer ring in pure tetranitromethane. As the concentration of the solution increased (1 : 4 and 1 : 2) the scattering at small angles also increased as before, and the outer ring increased in brightness and definition, though its position remained unaltered (3·02 A.U.). More concentrated solutions were not examined.

Hexamethylene tetramine and Solutions :—The substance has been shown to belong to the body-centred cubic system[1] containing two molecules to the unit cell. The powder pattern gave strong reflections corresponding to 4·95, 2·86 and 2·02 A.U. from the 110, 112 and 111 planes respectively. The most concentrated solution examined (1 : 1·25) gave an inner ring very much broadened out and a distinct outer ring corresponding to 2·86 A.U. Some amount of scattering was present outside this ring also. At a concentration of 1 : 3, the inner ring had broadened out more, while the outer ring had contracted slightly, and was also more intense. The space

Dickinson and Raymond, J. Am. Chem. Soc., 45, 22 (1923).

between the two rings was not at all clear. At 1 : 4, the inner ring though still very broad, showed a maximum near its outer edge, while the outer ring had contracted still further. The separation between the two rings was barely visible. At 1 : 6, the two rings had merged into one another, and at 1 : 10 only the water ring was visible, with some scattering inside the ring. In all these cases, the scattering at small angles though considerable, was not at a maximum. The latter always appeared at a larger angle, though it became broader and more diffuse with increasing dilution. This is analogous to the behaviour of phenol, trimethylcarbinol and piperidine solutions, and has already been discussed in a previous communication.[1]

3. Discussion of Results.

Tetranitromethane and Solutions :—The crystal structure of this substance has been examined by Mark and Noethling, who have shown from a powder pattern that it belongs to the cubic system containing four molecules to the unit cell, the side of the latter being 9·2 A.U. The lines of the powder pattern as given by the authors are tabulated below :—

TABLE I.

Tetranitromethane (Powder pattern).

Plane.	Spacing in A.U.	Intensity.
100 (2)	4·60	Strong
110 (2)	3·18	Weak
111 (2) β ⎫	2·85	Strong
113 ⎭		
111 (2)	2·72	,,
100 (4)	2·30	Medium
133	2·12	Weak
112 (2) ⎫	1·88	V. strong
110 (4) β ⎭		
111 (3)	1·78	Weak
110 (4)	1·64	V. strong
110 (6)	1·08	Medium
120 (4)	1·03	,,

Krishnamurti, Ind. J. Phys., 3, iii, 331 (1928)

The two rings obtained in the present investigation for the liquid, have the spacings given below:

(1)	5·49 A.U.	Strong
(2)	3·02 ,,	Weak

while in a dilute solution in benzene or cyclahexane, a strong scattering at small angles and a weak maximum at about 3·02 A.U. were obtained. Comparing first the patterns for the solid and liquid, it is found that the strongest spacings of the powder pattern do not appear in similar positions in that of the liquid. Moreover, the absence in the former of the first order spectrum of the 111 plane which will have a spacing comparable with the first liquid ring is very significant. If all the four molecules composing the unit cell had maintained the same positions as they did in the solid, then we should have expected strong rings in the liquid pattern with spacings of 4·60, 2·85, 2·72, 1·88 and 1·64 A.U. or in their immediate neighbourhood. As it is, only two rings are obtained for the liquid having the spacings 5·49 A.U. and 3·02 A.U., with no third maximum even. Hence it follows that there is some arrangement of the molecules in the liquid differing considerably from what is present in the solid.

The origin of the principal ring in the liquid patterns has been discussed by Raman and Ramanathan, who suggested that the wavelength λ_0 of the peak in the 'structural spectrum' is practically identical with the mean distance between neighbouring molecules in the liquid. For an ideal gas, this mean distance is $0·554n^{-\frac{1}{3}}$, where n is the number of molecules per unit volume. For a simple cubical arrangement of the molecules,[1] this distance is equal to $1·n^{-\frac{1}{3}}$ while for the closest packing it is $1·123n^{-\frac{1}{3}}$. The authors have considered in detail only the case of a simple cubic array of molecules

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[1] C. V. Raman, Phil. Mag., 47, 671 (1924).

when deducing the position of maximum intensity in the structural spectrum.

The arrangement of the molecules may however depart from this simple cubic arrangement. Since the molecular forces which determine the form in which a substance should crystallise are present to a great extent in the liquid also, we can assume that the space array in the liquid is similar to that of the crystal, but modified by thermal fluctuations and changes in density. Hence the distance between neighbouring molecules reduces itself to the distance between the planes in which the points of the structure lattice are most densely packed. Taking the case of a simple cube, it will be evident that in the crystal it is the 100 plane which acts most effectively in reflection. The spacing of this plane is simply the length of the unit cube, and since the unit cell contains only one molecule it will be equal to $1 \cdot 00n^{-\frac{1}{3}}$. The next case is that of the body-centred cube, where the plane which contains the largest number of molecules is the 110 plane. The spacing of this plane will be $0 \cdot 707 \times (2n)^{-\frac{1}{3}}$ since there are two molecules per unit cell, or equal to $0 \cdot 97n^{-\frac{1}{3}}$. In the next case of the face-centred cube, the plane containing the largest number of molecules is the 111 plane. The spacing of the planes is $0 \cdot 577 \times (4n)^{-\frac{1}{3}}$ or $0 \cdot 92n^{-\frac{1}{3}}$. From Table II we can see that the values of k given in the last column are approximately the same as given above. The crystal structure of tetranitromethane has not been fully investigated, but the ratio of $0 \cdot 94$ shown in the table suggests that the 111 planes may contain the largest number of molecules per unit area. In the case of argon which belongs to the face-centred cubic system,[1] the ring for the liquid appears also at a spacing very nearly equal to that of the 111 planes of the crystal. The crystal structure of carbon tetrachloride is not known, but judging from the analogous case of carbon tetraiodide, it is

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[1] Simon and Simson, Z. f. Phys., 25, 160 (1924).
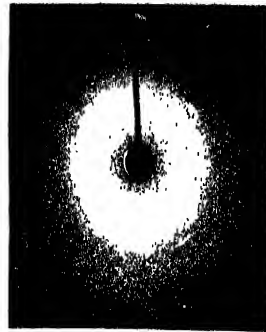
HEXAMINE POWDER   SOLUTION, 1:1·25
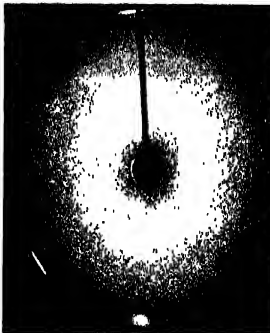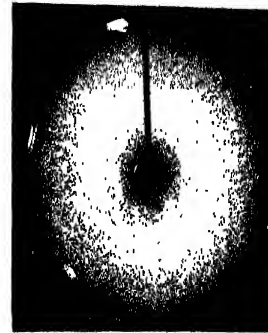
SOLUTION, 1:3   SOLUTION, 1:4

SOLUTION, 1:6   WATER

X-RAY DIFFRACTION IN SOLUTIONS.

TABLE II.

| Liquid. | Col. 1. | Col. 2. | Col. 3. | Col. 4. | |
	I ring in A.U.	II ring in A.U.	III ring in A.U.	$\left(\frac{m}{d}\right)^{-\frac{1}{3}}$ in A.U.	$\dfrac{\text{Col. 1}}{\text{Col. 4}} = k$
Tetranitromethane ...	5·49	3·02	...	5·82	0·94
Carbon tetrachloride[1]	5·30	2·90	...	5·43	0·98
Argon[2] ...	3·30	1·86	...	3·60	0·92
Mercury[3] ...	2·85	1·41	1·04	2·90	0·98

probable that it belongs to the simple cubic system, and hence will fit in with the observed value of k which is nearly equal to unity.

The question next arises as to the origin of the outer ring in tetranitromethane. A study of its solutions in benzene and cyclohexane was undertaken in order to make this point clear. A dilute solution of tetranitromethane in any of the above solvents gave a pattern with a strong scattering at small angles, showing thereby that the dissolved molecules were distributed at random in the solution. Further, with increasing concentration of the solution, the inner scattering increased in intensity. Even in dilute solutions (1:6 by weight or 1 mol : 14 mols.) of cyclohexane, a faint and diffuse maximum was observed at an angle of 29·5° corresponding to a spacing of 3·02 A. U. This became stronger and clearer at greater concentrations. Similarly also with benzene solutions, the inner corona as well as the outer faint maximum at about 3·06 A. U. were

[1] Sogani, loc. cit.
[2] Keesom and Smedt, Proc. Roy. Soc. Amst., 25, 118 (1923).
[3] J. A. Prins, Physica, 6, 315 (1926).

observed at a concentration of 1 : 3, and in a more concentrated solution (1 : 1·1 by weight or 1 mol. : 3 mols.) the benzene ring had almost joined up with the centre, while the outer maximum was stronger and clearer than before.

In order to understand the pattern given by the solute in a dilute solution, let us first consider the diffraction by a spherical particle whose dimensions are comparable with λ, and which has a dielectric constant nearly equal to unity. If R be the radius of the sphere, it has been shown that the intensity P at any angle θ is proportional to

$$\left(\frac{\sin m - m \cos m}{m^3} \right)^2,$$

where

$$m = \frac{4\pi \, R \sin \frac{\theta}{2}}{\lambda}.$$

The first expression will have a maximum when m is equal to zero and also when it is nearly equal to 2π. In the latter case,

$$4\pi \, R \sin \frac{\theta}{2} = 2\pi \, \lambda$$

$$\text{Or, } \sin \frac{\theta}{2} = \frac{\lambda}{2R}.$$

Taking the diameter of the molecule as approximately equal to $\left(\frac{m}{d} \right)^{-\frac{1}{3}}$ where m is its mass and d the density, in the case of tetranitromethane we have :

$$2R = 5·82 \text{ A.U.}$$

$$\sin \frac{\theta}{2} = \frac{1·54}{5·82} = 0·2646$$

Or, $\theta = 30·7°$ for copper Kα radiation.

The observed value for the second weak maximum in dilute solutions is 29·6°, and is in fair agreement with the calculated value.

Similarly, we have in the case of hexamethylene tetramine,

$$2R = 5·57 \text{ A. U.}$$

$$\theta = 32·1° \text{ for Cu K}\alpha \text{ radiation.}$$

It is interesting to note that in this case also, the position of the second maximum in the patterns of its solutions is at about 31·2°, and thus agrees with the calculated value. The first maximum, due to some cause, does not appear at very small angles in a dilute solution; but the presence of the second maximum is quite clear in 1 : 1·25 and 1 : 2 solutions, though in more dilute solutions its presence is obscured by the water ring which then becomes prominent. That the outer ring in 1 : 3 and 1:4 solutions is made up of these two maxima superimposed on one another is proved by the shifting of the water ring (27·3°) outwards (to about 29°—30°) in these solutions.

4. *Origin of the outer halo.*

Considering the patterns given by the pure liquids, it can be seen from Table II that a faint outer ring is present also in the patterns of liquids containing symmetrical molecules. The origin of this outer ring has been discussed by Sogani in the case of carbon tetrachloride as mentioned previously. At first sight, it appears as if it is merely a second order of the first prominent ring. But the spacing of the outer ring in many of these cases is not exactly half of that of the first ring, but varies from 0·50—0·58. This fact is very significant, and shows that it is not merely the second order spectrum.

In the previous section, we have considered the diffraction by spherical particles distributed at random. Let us now consider what will happen if the particles possess a fairly ordered arrangement as found in a liquid, or a completely regular one as in the case of a crystal.

Suppose we divide up a unit volume of a fluid into a number of thin slices, and let us suppose also that each slice is only one molecule thick, the distance d between the two slices being so chosen that $2d \sin \frac{\theta}{2} = \lambda$. Since the effects of the particles in one slice will all add up, and will agree in phase with those of the next slice, a maximum will be obtained at an angle θ. Several other maxima are also possible when the phase difference is 2λ, 3λ and so on, if the particle contains all its scattering matter concentrated at a point. But in actual practice, it is impossible to have such points only, and the influence of the dimensions of the particles on the various orders of the spectrum should then be considered.

Let us first take the case of a particle, the diameter of which is exactly equal to the distance d between the two slices. If the particles be sharply bounded, we can have a second maximum due to the structure of the particle. This will occur in the direction θ' such that $4\pi R \sin\frac{\theta'}{2} = 2\lambda$, and hence if $2R = d$, this effect will occur at the same angle as the second order spectrum. This corresponds to the case of a simple cubic lattice, where the molecules are situated at all the corners of the cube.

Let us now consider a case where $2R > d$. In this case, it is evident that the two effects would not appear at the same angle. For,

$$2R = \frac{\lambda}{\sin \frac{\theta'}{2}} \qquad d = \frac{\lambda}{\sin \frac{\theta}{2}}$$

Since $2R \gtrless d$, $\theta \gtrless \theta'$.

In the case of a body-centred cubic structure, the plane containing the largest number of molecules per unit area is the 110 plane, and its spacing will be $0 \cdot 97 n^{-\frac{1}{3}}$. The minimum distance between two molecules in the unit cell will be that from the centre of the cube to the corner or $1 \cdot 09 n^{-\frac{1}{3}}$. The latter will be equal to 2R, and this is greater than the value of $d (= 0 \cdot 97 n^{-\frac{1}{3}})$. In the case of the face-centred cubic lattice, the distance between the 111 planes is $0 \cdot 92 n^{-\frac{1}{3}}$. The minimum distance between two molecules in the cube will be that from the centre of the face to the corner or $1 \cdot 123 n^{-\frac{1}{3}}$. The following table shows these relationships clearly:—

TABLE III.

(1)	(2)	(3)	(4)	(5)	(6)
Unit cell	Strongly scattering plane	Spacing of (2) $\times n^{-\frac{1}{3}}$	Min. dist. of mols. in cell $\times n^{-\frac{1}{3}}$	Spacing of max. due to struct. $\times n^{-\frac{1}{3}}$	$\dfrac{\text{Col. (5)}}{\text{Col. (3)}}$
Simple cube.	100	1·00	1·00	0·50	0·50
Body-centred cube.	110	0·97	1·09	0·545	0·56
Face-centred cube.	111	0·92	1·123	0·56	0·61

It is interesting to note that in the case of liquid argon, the ratio actually obtained of the spacing of the outer ring to that of the inner is 0·58, a value which agrees fairly with that given above for a face-centred cube.

This also helps us to understand why in a dilute solution an outer maximum should be present ; for, though the second order effect might vanish, the maximum due to the structure factor of the molecule might still persist.

5. Experimental.

The usual Debye-Scherrer method using the copper K_α radiation was employed. The cell for holding the liquid had to be made of pure gold to enable it to withstand the corrosive

action of tetranitromethane. Mica windows were used as usual for the cell. The distance between the photographic plate and the liquid was 2·60 cms. About two hours' exposure at 5 milliamperes sufficed for each liquid.

The tetranitromethane was supplied by the British Drug Houses. The solutions with benzene were coloured yellow, but with cyclohexane they were colourless. The requisite quantities of the two liquids were weighed out, mixed and immediately a portion was transferred to the cell.

The hexamethylene tetramine was Merck's pure variety which was dissolved in distilled water in the requisite proportions. The powder pattern reproduced in this paper was taken with a narrower beam, the distance between the powder and the plate being also slightly different. Otherwise, all the different liquids were examined under identical conditions.

The results obtained are tabulated below. The proportions given refer to parts by weight of the solute and solvent respectively. The spacings were calculated as usual from the Bragg formula

$$d = \frac{\lambda}{2 \sin\frac{\theta}{2}}$$

λ in this case being equal to 1·54 A. U.

TABLE IV.

Tetranitromethane—Cyclohexane Solutions.

Liquid	Inner Ring		Outer Ring	
	θ in deg.	λ in A. U.	θ in deg.	λ in A. U.
Tetranitro-methane	16·1	5·49	29·6	3·02
1 : 2 Soln.	16·6	5·33	,,	,,
1 : 4	,,	,,	,,	,,
1 : 6	17·1	5·18	,,	,,
Cyclohexane	,,	,,	...	...

TABLE V.

Tetranitromethane—Benzene Solutions.

Tetranitro-methane	16·1	5·49	29·6	3·02
1 : 1·1 Soln.	17·3	5·12	29·1	3·06
1 : 3	17·6	5·03	·,	,,
Benzene	18·1	4·89	...	...

TABLE VI.

Hexamethylene tetramine Solutions.

Solution	Inner Ring		Outer Ring	
	Inner margin in A.U.	Outer margin in A. U.	θ in deg.	λ in A. U.
1 : 1·25	8·5	4·03	31·2	2·86
1 : 2	9·8	4·12	30·8	2·90
1 : 3	9·8	3·12	30·0	2·97
1 : 4	9·8	max. at 4·12	28·7	3·11
1 : 6	7·7	3·02	...	...
Water	...	...	27·3	3·26

In conclusion, the author wishes to thank Prof. C. V. Raman, F.R S., for the valuable help and criticism received during the course of this work.

Note added to proof :—Dilute solutions of carbon tetra-chloride in cyclohexane (1 : 6·5 and 1 : 4 by weight) were also examined by this method. A longer exposure (about 4 hours) was however necessary. The patterns showed the presence of distinct maxima at an angle of 30·9 corresponding to a spacing of 2·9 A. U., a value which is the same as that obtained for the pure liquid. Hence, in this case also, the outer ring of the liquid should be due to the structure factor of the molecule.

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The Spectrum of Trebly Ionised Thallium (Tl. IV)

By

P. Pattabhiramayya, M.A.

In two recent papers McLennan,[1] McLay and Crawford, described the spectra of Au. II and Hg. III. The present paper deals with the isoelectronic spectrum of Tl. IV. The regular doublet law of X-ray spectra given by Prof. Sommerfield and modified for optical spectra,

$$\Delta \nu (^1D_1 - {}^1D_s) = \xi (Z - s)^4,$$

the constant ξ involving the constants R, a, n, l, which has been found to be extremely fruitful in the investigation of isoelectronic spectra has been employed for the extrapolation of the separations of the sub-levels which are of rather very large magnitude comparable to the total level separations of the homologous spectra of the normal type. The principle of a continuous and even variation of the interval ratios between sub-levels has been useful in the fixing of sub-level separations to within narrow limits.

The characteristic terms that have been recognised in the arc spectra of Ni, Pd, and Pt are all analogous, and the same

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[1] Trans. Roy. Soc., Canada, Vol. 22, sec. 3, 1928.

system of terms has been found in the progression Ni I, Cu II, Zn III, etc., Pd I, Ag II, Cd III, etc., Pt I, Au II, Hg III. The system of terms are based on the electron configuration built upon the ion $d.^9$ By adding an s electron in the orbit of the next higher total quantum number the terms that would arise are $^{3\&1}D$; and by adding a p electron, the terms $^{3\&1}P.D.F$ would arise. By adding a d electron in the previous quantum orbit making the configuration d^{10} the term that would arise would be a ^1S. There may be intercombinations between this ^1S term and the $^{3\&1}P$ term, which would result in three lines, and the ^1S term has been located in some spectra but it is not possible to locate this term with the data available, in the spectrum of Tl. IV. The combinations between the terms arising from the configurations $5d,^96s$ and $5d,^96p$ have been identified and the terms evaluated based on the commonly adopted method of giving the value zero to the deepest term found, viz., $^0D_3$. The term values are thus only relative.

The wave-length material used in this investigation is that of Caroll.[2]

Table I gives the scheme of Multiplets formed by the combination of terms. The wave number of the lines has been given and the intensity of the lines is given in small brackets. The table also gives the term values based upon the assumption that the level $^0D_8$ is zero. The sub-level separations are also given.

The ^3D, $^{3\&1}\overline{D}$ and ^3D, ^1F groups have been partially recorded as the wave-length material available was insufficient towards the extreme ultra-violet to locate the lines. But the terms have been based on the recurrence of pairs with frequency differences in the available data corresponding to their proper positions.

Table II gives the progression of the regular doublet law in the homologous spectra of Pt I, Au II, Hg III and Tl IV.

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[2] Phil. Trans., Vol. 225, pp. 410-15.

Table III gives the progression of the difference in sub-levels in the spectra of the homologous series of elements.

Table IV gives the progression of the $^{3\&1}P$, $^{3\&1}D$ multiplet in the sequence of the spectra and illustrates how well the irregular doublet law is followed in the spectra of even the heaviest elements.

Table V gives the list of lines classified in this investigation.

The correctness of the above scheme depends to a very large extent on the similarity of the term and multiplet disposition in the sequence of spectra. The intensities of the lines in the multiplets are in decent accord with the rules following the selection principle of the azimuthal and internal quantum numbers. Over and above the lines in the inaccessible region, only three lines have not been found and they are some of the relatively weaker lines expected in the multiplets.

In conclusion I wish to take this opportunity to express my grateful thanks to Dr. T. Royds, Director of the Kodaikanal Observatory, for the facilities afforded to me and to Dr. A. L. Narayan for the active interest and continued help and guidance given to me in the progress of this work.

TABLE I.

Term → $5d^96s$	³D₃	Δ	³D₂	Δ	³D₁	Δ	¹D₂
↓ $5d^96p$ Value	0	3586	8586	15745	19331	3902	23233
³P₂ 72584	72582 (7)		68996 (5)		53254 (1)		49353 (1)
Δ 19856							
³P₁ 92440			88848 (4)		73114 (3)		69209 (1)
Δ 10111							
³P₀ 102551					88220 (3)		
Δ −3197							
¹P₁ 99354			95768 (3)		80028 (2)		76150 (1)
³F₄ 92617	92617 (6)						
Δ −17841							
³F₃ 74776	74784 (4)		71195 (3)				51530 (0)
Δ 18168							
³F₂ 92944	...		89874 (3)		78606 (5)		69701 (6)
Δ 16291							
¹F₃ 109235	...		...				86002 (4)
³D̄₃ 97004	97006 (3)		93416 (4)				...
Δ −5648							
³D̄₂ 91356	91353 (0)		87773 (5)		...		68046 (2)
Δ 23568							
³D̄₁ 114924	...		...		95600 (1)		91684 (4)
Δ −2378							
¹D̄₂ 112546	...		...		98218 (0)		89809 (2)

TABLE II.

	Element.		³D₁ − ³D₂	$\sqrt{\Delta\nu/0.00778}$	s
78	Pt I	...	10132	33·78	44·22
79	Au II	...	12727	35·76	43·24
80	Hg III	...	15556	37·60	42·40
81	Tl IV	...	19331	39·70	41·30

TABLE III.

Term.	Pt I.	Au II.	Hg III.	Tl IV.
$^3D_3$				
Δ		2601	3179	3586
$^3D_2$				
Δ	10182	10125	12377	15745
$^3D_1$				
Δ		1855	2679	3902
$^1D_2$				
$^3P_2$				
Δ		10351	15057	19856
$^3P_1$				
Δ		9210	7948	10111
$^3P_0$				
Δ		−954		−3197
P_1				
$^3F_4$				
Δ		−7492	−12366	−17841
$^3F_3$				
Δ		11656	15300	18168
$^3F_2$				
Δ		9040	11560	16291
$^1F_3$				
$^3D_3$				
Δ		−1613	−3052	−5648
$^3D_2$				
Δ		12529	17928	23568
$^3D_1$				
Δ		858	−1890	−2878
$^3D_2$				

TABLE IV.

5d⁹6s. / 5d⁹6p		³D₃	Δ	³D₂	Δ	³D₁	Δ	¹D₂	Δ
³P₂	Au II	48014		45413		35287		33432	
			12584		12108		9856		9032
	Hg III	60698		57521		45143		42464	
			11884		11475		8111		7889
	Tl IV	72572		68996		53254		49353	
P₁	Au II			55763		45638		48783	
					16814		14560		13738
	Hg III			72577		60198		57521	
					16271		12916		11688
	Tl IV			88848		73114		69209	
³P₀	Au II					54848			
	Hg III					?			
	Tl IV					83220			
¹P₁	Au II			64018		53893		52038	
					16517		14256		13429
	Hg III			80535		68149		65467	
					15228		11879		10683
	Tl IV			95763		80028		76150	

TABLE V.

λ. I. A. (vac).	Int.	ν	Classification.
2026·2	1δ	49353	¹D₂ — ³P₂
1940·6	0	51530	¹D₂ — ³F₂
1877·8	1	53254	³D₁ — ³P₀
1469·59	2	68046	¹D₂ — ³D̄₂
1449·37	6	68996	³D₂ — ³P₂
1444·9	1	69209	¹D₂ — ³P̄₁
1434·71	6	69701	¹D₂ — ³F₂
1404·60	8	71195	³D₂ — ³F₂
1377·75	7	72582	³D₂ — ³P₂

TABLE V.—Contd.

λ. I.A. (vac).	Int	ν	Classification.
1367·72	3	73114	$^3D_1 - ^3P_1$
1358·58	5	73606	$^3D_1 - ^3F_2$
1337·19	4	74784	$^3D_2 - ^3F_3$
1313·20	1	76150	$^1D_2 - ^1P_1$
1249·56	2	80028	$^3D_1 - ^1P_1$
1201·64	3	83220	$^3D_1 - ^3P_0$
1162·77	4	86002	$^1\bar{D_2} - ^1F_3$
1139·30	5	87773	$^3D_3 - _3\bar{D_2}$
1125·52	4	88848	$^3D_3 - ^3P_1$
1119·71	2	89309	$^1D_2 - ^1\bar{D_2}$
1118·89	2	89374	$^3D_2 - ^3F_2$
1094·65	0	91353	$^3\bar{D_2} - ^3\bar{D_3}$
1090·70	4	91684	$^1D_2 - ^3\bar{D_1}$
1079·71	6	92617	$^3D_3 - ^3F_4$
1072·75	0	93218	$^3D_1 - ^1\bar{D_2}$
1070·48	4	93416	$^3D_2 - ^3\bar{D_2}$
1046·02	1	95600	$^3D_1 - ^3\bar{D_1}$
1044·25	3	95763	$^3D_2 - ^3P_1$
1030·86	3	97006	$^3D_2 - _3\bar{D_2}$

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Series Spectrum of Se IV

By

P. Pattabhiramayya, M.A., and A. S. Rao

According to the present-day spectral theories the term structure of Se IV is similar to that of the analogous atoms and ions Ga I, Ge II, and As III which have been analysed to some extent. Their term structure is in complete accord with that predicted from the Hund theory. The term structure is as follows :—

Electron configuration.	Terms predicated.
s^2p	^2P
s^2s	^2S
s^2d	^2D
s^2f	^2F
	etc.
$s\ p^2$	$a^4P\ \ a^2D\ \ a^2P\ \ a^2S$
$s\ p\ s$	$b^4P,\ b^2P$
p^3	$c^4S\ \ c^2P\ \ c^2D$

In a previous paper we have reported the regularities in the spectra of As III and Sb III. Analogy with these spectra indicated the position and frequency difference of the fundamental doublets in this spectrum. The following note presents regularities in the spectrum of Se IV.

The spark spectrum of Se has been measured by Exner and Haschek and by others and more recently by Messerchmitt

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from λ 5898 to λ 2340 and in the vacuum grating region by Humphrys and Sawyer whose unpublished data are kindly made available to the authors for use.

The results of this analysis are given in Tables I to V. Table I gives a list of the lines that have entered into the present classification. The terms and the term values found are also given.

Table II gives the variation of the logarithms of the difference in the values of $^2P_1$ and $^2P_2$ with the logarithms of the net nuclear charge, viz., the logarithms of the natural numbers 1, 2, 3, etc. It is found that there is linear variation of the logarithms of doublet separation and the logrithms of the net nuclear charge.

Table III gives the comparative positions of some of the prominent members in the spectra of Ga I, Ge II, As III and Se IV.

Table IV gives the progression of the terms in the spectra of these elements. The term values have been divided by 1, 4, 9, respectively for purpose of comparison. The progression is statisfactory except in the case of 2^2S_1, where a rather abnormal rise is found. The absence of any other satisfactory pair in the required region necessitated the acceptance of this abnormal value for the term. The term values have all been calculated on the assumption $I^2G = 70400$ ($\frac{\nu}{c^2} - 4400$). The largest term found is $1^2P_1 - 354,161 cm^{-1}$.

Table V gives some unclassified pairs with frequency differences $4374 cm^{-1}$ with their probable classification.

We desire to acknowledge our indebtedness to Dr. T. Royds, the Director of the Observatory, for the facilities afforded and to Dr. A. L. Narayan for his active interest and guidance in this work.

KODAIKANAL OBSERVATORY.

March, 1929.

TABLE I

Classification.	λ (Vac)	I	ν	Δ ν	Term	Value	Δ ν
1²P₁—1²S₁	722·76	4	138359		1²P₁	354161	
1²P₂—1²S₁	746·36	4	133984	4375	1²P₂	349788	4373
1²P₂—1²D₂	690·35	0	144854		1²S₁	215802	
1²P₂—1²D₃	687·73	2	145406	552	1²D₂	204934	
1²P₁—1²D₂	670·12	7	149227	4373	1²D₃	204383	551
1²P₂—a²P₁	817·00	2	122399		1²F₃	112132	
1²P₁—a²P₁	799·80	4	126775	4376	1²F₄	111946	186
1²P₂—a²P₂	803·80	3	124409	2010	1²G	[70400]	
1²P₁—a²P₂	776·50	4	128783	4374	2²P₁	182849	1127
1²P₂—a²D₂	1001·64	5	99836		2²P₂	181722	
1²P₂—a²D₃	996·70	8	100331	495	2²S₁	142118	
1²P₁—a²D₂	959·60	8	104210	4374	a²P₁	227386	2008
1²D₃—1²F₃	1084·00	1	92251		a²P₂	225378	
1²D₃—1²F₄	1081·81	2	92439	188	a²D₂	249951	494
1²D₂—1²F₃	1077·56	4	92802	551	a²D₃	249457	
1²F₃—1²G	2396·23	0	41732				
1²F₄—1²G	2406·96	2	41546	186			
a²D₂—2²P₂	...	...	[68244]				
a²D₃—2²P₂	1475·48	0	67775	469			
a²D₂—2²P₁	1489·92	0	67118 (obs.) 67103 (cal.)	1126			
2²P₁—2²S₁	2455·13	2	40731				
2²P₂—2²S₁	2524·97	2	39605	1126			
	λ (air)	...					
1²S₁—2²P₂	2933·42	5	34080·0	1127·2			
1²S₁—2²P₁	3099·76	3	32952·8				
1²D₂—2²P₂	4804·23	3	23226·5(obs.) 23212 (cal.)	552·8			
1²D₂—2²P₂	4409·16	3	22673·7(obs.) 22661 (cal.)	1126·2			
1²D₃—2²P	4523·59	5	22100·2 22085 (cal.)				

TABLE II

	Ga I	Ge II	As III	Se IV
$\triangle \nu\ 1^3P_{1,2}$	826	1768	2946	4374
$\log \triangle \nu\ 1^3P_{1,2}$	2·917	3·247	3·469	3·641
$\triangle \nu\ 2^3P_{1,2}$	108	360	723	1126
$\log \triangle \nu\ 2^3P_{1,2}$	2·033	2·556	2·859	3·052
log.net charge	0	0·301	0·477	0·602

TABLE III

	Ga I	Ge II	As III	Se IV
$1^3P_1 - 1^3S_1$	24788	62402	102604	138359
$1^3P_1 - 1^3D_2$	34782	80831	109782	149227
$1^3D_2 - 1^3F$	...	19481	46464	92802
$1^3P_1 - a^3P_1$	...	91012	113941	126775
$1^3P_1 - a^3D_2$	...	65014	99944	104210
$a^3D_2 - 2^3P_1$	...	[13992]	27428	67118
$1^3S_1 - 2^3P_2$	[8265]	16603	25487	32953
$2^3P_1 - 2^3S_1$	...	15778	31431	40731
$1^3D_2 - 2^3P_1$	...	...	17586	22100

TABLE IV

Term	Ga I	Ge II	As III	Se IV
1^2P_1	48380	32357	24469	22135
1^2D_2	13598	12149	12271	12809
1^2S_1	23592	16757	13069	13488
2^2P_1	15326	12606	10917	11428
2^2S_1	10795	8662	6905	8882
a^2P_1	...	9604	11809	14211
a^2D_2	...	16104	13865	15622
1^2F_2	...	7278	7108	7008

TABLE V
Unclassified pairs.

λ (Vac)	I	ν	△ ν	Probable classification.
634·54	4	157595		
652·66	4u	153219	4376	$1^2P_{1,2}-a^2S_1$
806·54	4u	123986		
836·10	3	119603	4383	
836·10	3	119603		
867·80	3	115234	4369	$1^2P_{1,2}-a^4P_2$
857·34	5	117049		
887·48	3	112679	4370	$1^2P_{1,2}-a^4P_1$

REVIEW.

Kurzer Leitfaden der Photochemie—By J. Plotnikow pp. 1-186 Published by Georg Thieme, Verlag, Leipzig. Price M 7.50 in paper covers, bound M. 8.50.

The book is intended specially for medical workers interested in light-therapy and photo-physiology, but will, it is believed, appeal to a much wider circle of readers. The author is Director of the Physico-Chemical Institute in the University of Zagreb and is a well-known authority on Photochemistry, having many earlier works on the subject to his credit. The book is illustrated by 40 diagrams and photographs explanatory of apparatus, methods and results in the study of radiation and its effects. The fundamental aspects of the subject as well as its applications are adequately dealt with. As can be expected from an author so thoroughly a master of his subject, the treatment is attractive and stimulating. The subject of photochemistry is very fundamental in modern scientific advance, and Prof. Plotnikow's introduction to it is heartily to be welcomed.

<div align="right">C. V. R.</div>